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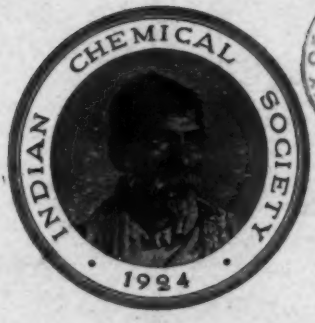

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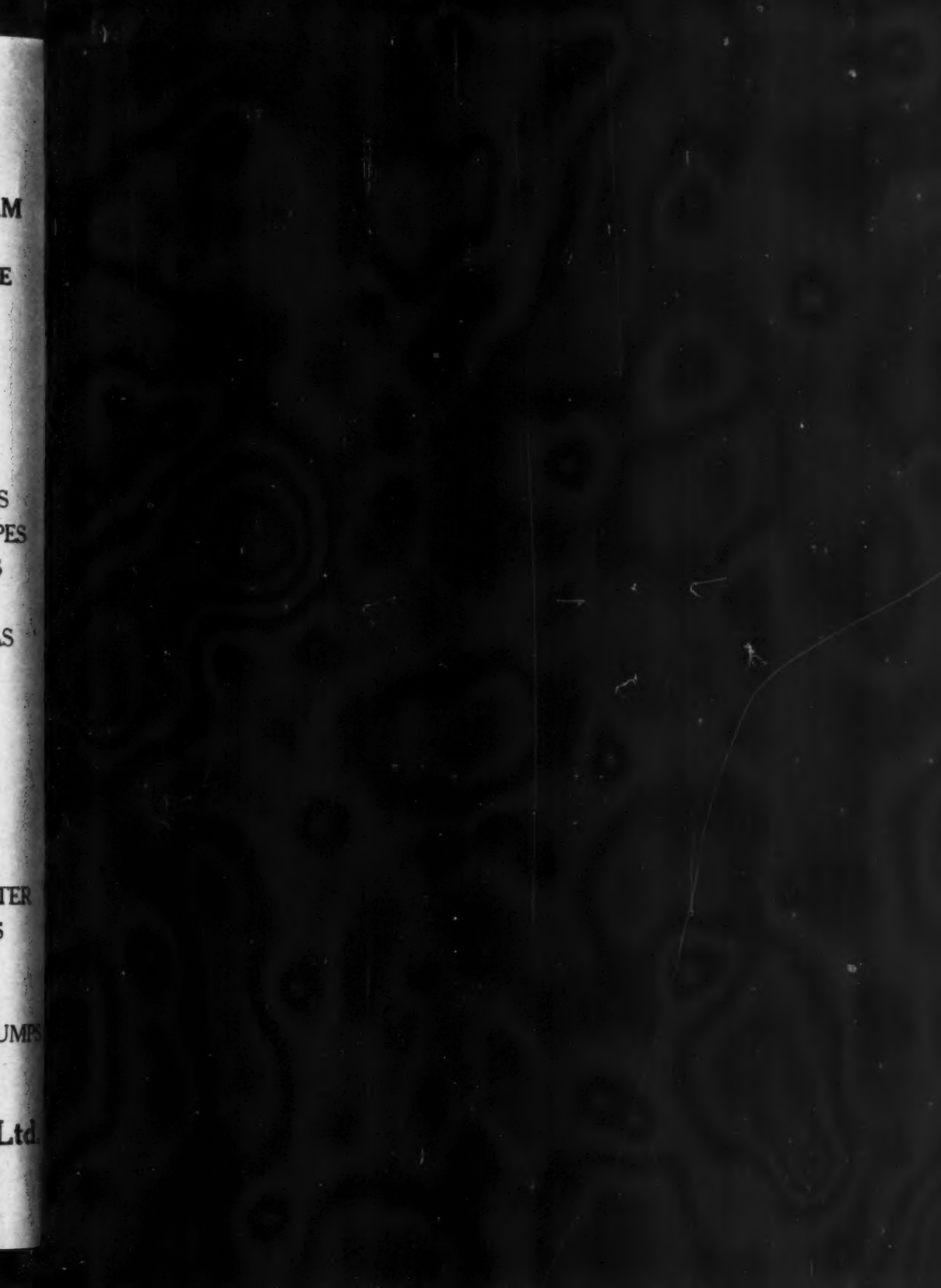

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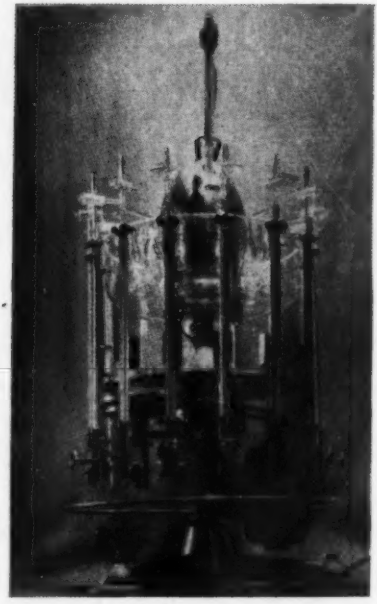

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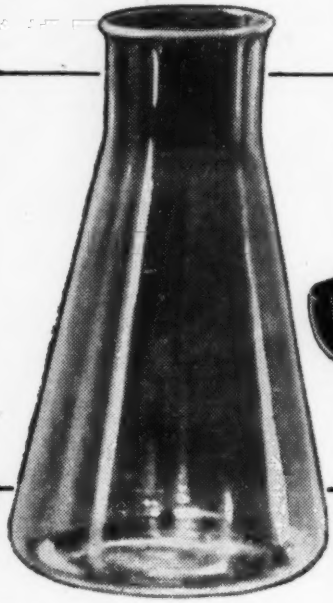

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FEBRUARY, 1961

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FOR AUTHORS ONLY

*Extracts from the "Style Guide for Chemists" by Fieser & Fieser will be published henceforth in each issue of this Journal so that authors may take advantage in improving the quality of their composition and presentation.

1.6. The short versus the long.

In the expression *in so far as*, the *in* usually is superfluous.

The following sentences can be shortened by the changes suggested :

Reduction of a ketone *in many cases* requires.....(*often* requires).

Yields are generally good, with a few examples of remarkably high conversion *in the case* of both aromatic and heterocyclic aldehydes (*of* both).

The results were inconclusive *owing to the fact that* the catalyst was contaminated. (Use *because*; do not say *because of contamination of the* catalyst.)

The word *of* often is used where it is not needed ; for example, it should be deleted from the following expressions :

.....all *of* the reactions described.....

.....all *of* the ketones in the series....(neither *of* nor *the* is needed).

But : *all of which* is correct.

2.1. A participial phrase must modify the subject intended.

Incorrect : Reasoning that the carbon atoms may not be in a plane, the puckered form was suggested by Sachse.

The participle *reasoning* modifies *form*, whereas it was *Sachse* who did the reasoning. Say : "Reasoning that ..... Sachse suggested....."

Incorrect	Correct
At the time unequipped for NMR spectroscopy, the sample was sent to Varian Associates.	At the time unequipped for NMR spectroscopy, we sent the sample to Varian Associates.
Coming off ahead of the ester, we noticed a band due to ketonic material.	We noticed a band due to ketonic material coming off ahead of the ester.
Being somewhat dirty, I was unable to return the flask to the store-room.	The flask being somewhat dirty, I.....(*better.* Since the flask was.....)
After washing, the precipitate was dissolved.....	After having been washed, the precipitate was.....
Viewed as an empirical expression we regard equation (1) as.....	Considered as an empirical expression, equation (1) is....
Before concluding, two general comments come to mind in reading this book.	Two general comments occurred to me in reading this book.

2.2. Do not dangle modifying phrases.

Incorrect : Following separation of the two layers, aniline is obtained in a pure condition by distillation of the benzene—aniline layer.

The phrase in italics does not modify *aniline* or other word of the sentence. It is unattached. It dangles.

After separating the two layers, I (or, the operator) obtained aniline.....

2.3. Relate a pronoun to its proper antecedent.

The antecedent or principal of a pronoun (*it, he, that, this, any, these, those,* etc.) must be clearly evident.

.....presents a situation different from those (any) considered above. (*Any* is both singular and plural).

Other syntheses, such as that (the preparation) from *n*-propyl alcohol, are more important.

The reaction between an aluminium alkoxide and a ketone can be reversed. This (reversibility) is the basis of the Oppenauer oxidation of a secondary alcohol to a ketone. (The antecedent of a pronoun should be a definite noun, not a general statement.)

*Extracts are printed with the consent of the Authors and Publishers of the book (Reinhold Publishing Corporation, U.S.A.)

[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

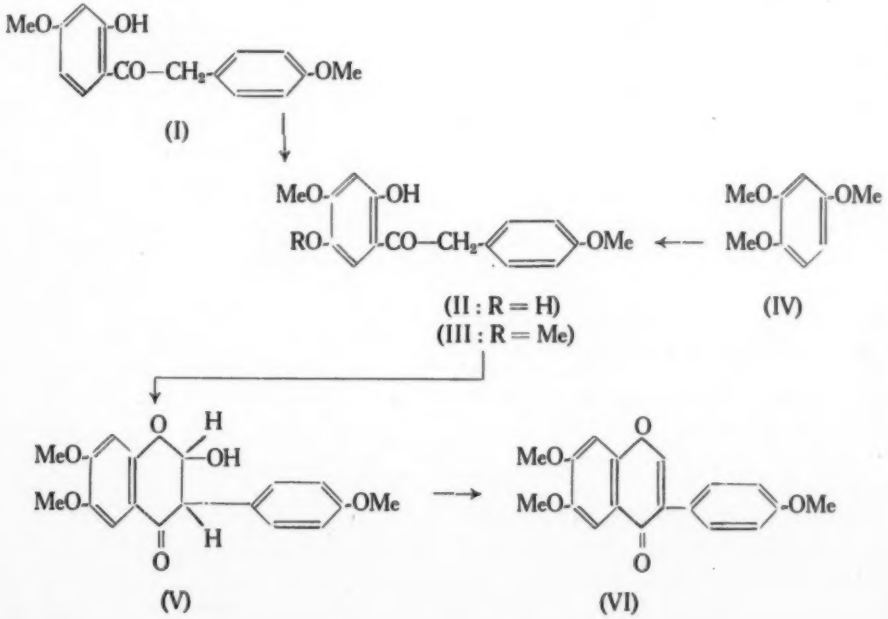
A New Synthesis of Afromosin

S. K. Arora, A. C. Jain, and T. R. Seshadri

Afromosin occurring in *Afromosia elata* has now been synthesised from 6,7,4′-trihydroxyisoflavone by stages of 7-benzylation, methylation, and debenzylation; it does not undergo nuclear methylation.

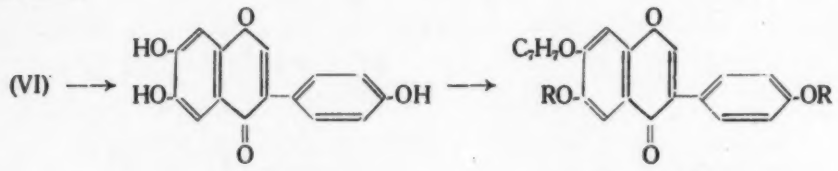
Afromosin, isolated recently by McMurry and Theng (*J. Chem. Soc.*, 1960, 1491) from the hardwood of *Afromosia elata* Harms, has been shown to be 6, 4′-dimethoxy-7-hydroxyisoflavone (X) by a detailed study of its derivatives and degradation products. The structure has further been confirmed by its synthesis as follows. It started from a difficultly accessible 4-methoxyresorcinol, which after condensation with *p*-methoxybenzyl cyanide yielded 2, 4-dihydroxy-5-methoxyphenyl-4-methoxybenzyl ketone. This deoxybenzoin was subjected to Farkas' method of isoflavone synthesis using zinc cyanide when afromosin could be isolated in nearly 20% yield.

An important feature of this compound is that it is a partial methyl ether with the 7-hydroxyl free. In isoflavones, this hydroxyl is known to be the most reactive (Narasimhachari and Seshadri, *Proc. Ind. Acad. Sci*, 1950, **32A,** 342) and this explains why many of the partial methyl ethers are 7-methoxy compounds. When this 7-hydroxyl is free, it should arise from earlier protection by some means, e.g., glycoside formation and subsequent methylation of other hydroxyl groups. In laboratory syntheses, instead of glycoside formation, benzylation has been conveniently used in a number of cases. A similar procedure has now been adopted for the convenient synthesis of afromosin.

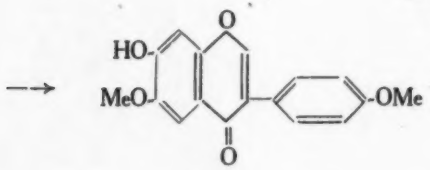


The first stage is the preparation of 6,7,4′-trimethoxyisoflavone (VI), which is conveniently made from the deoxybenzoin (III) by condensation with ethyl formate in presence of sodium. The initial product of this reaction is a 2-hydroxyisoflavanone (V), which with acetic anhydride undergoes dehydration to provide the required isoflavone. The deoxybenzoin (III) itself was obtained in two ways. The first and better method consists of the Friedel-Crafts reaction using 1, 2, 4-trimethoxybenzene (IV) (Müller *et al.*, *J. Org. Chem.*, 1954, **19,** 472) and *p*-methoxyphenylacetyl chloride (Kindler, *Arch. Pharm.*, 1927, **265,** 389), and the second method involves alkaline persulphate oxidation of the easily made phenylbenzyl ketone (I) (Badcock *et al.*, *J. Chem. Soc.*, 1950, 2961) and subsequent partial methylation. It agrees in its properties with the sample prepared by McMurry and Theng (*loc. cit.*) by the Hoesch reaction using 3, 4-dimethoxyphenol and 4-methoxybenzyl cyanide.

Demethylation of 6, 7, 4′-trimethoxyisoflavone (VI) could best be effected with anhydrous aluminium chloride and benzene; McMurry and Theng (*loc. cit.*) used hydriodic acid and phenol. The later steps in the synthesis of afromosin are partial benzylation in 7-position, methylation, and debenzylation (VIII-X). The synthetic product has all the properties reported for the natural afromosin.



(VII) (VIII : R = H) (IX : R = Me)



(X)

McMurry and Theng reported that when afromosin was methylated using methyl iodide, potassium carbonate, and acetone, they obtained a product different from *O*-methylafromosin (VI) and considered it to be a *C*-methyl derivative. Except in the case of carbonyl derivatives of phloroglucinol, this method does not effect *C*-methylation, and particularly no case is known so far in the flavonoid series. Further, afromosin does not have the necessary structure for *C*-methylation (Jain and Seshadri, *J. Sci. Ind. Res.*, 1955, **14A,** 227; *Quart. Rev.*, 1956, **10,** 169). Hence we have examined this point and found that afromosin forms only the *O*-methyl derivative (VI). As a parallel case, 6, 7-dihydroxyisoflavone has also been examined and found to yield only the *O*-methyl derivative.

EXPERIMENTAL

Ultraviolet absorption data were taken in methanol solution (unless otherwise stated).

2, 5-Dihydroxy-4-methoxyphenyl-4-methoxybenzyl Ketone (II).—2-Hydroxy-4-methoxyphenyl 4-methoxybenzyl ketone (I) was prepared by methylation of 2, 4-dihydroxyphenyl 4-methoxybenzyl ketone using dimethyl sulphate (1.1 *M*) (Badcock *et al.*, *loc. cit.*, used methyl iodide) and then

used for oxidation as follows. To an ice-cooled and well-stirred solution of the deoxybenzoin (2.72 g.) in aqueous KOH (2.8 g./50 c.c.) and pyridine (10 c.c.) was added potassium persulphate (3 g.) in water (30 c.c.) dropwise during 2 hours. After stirring for another 2 hours in an ice bath and subsequently leaving it overnight at room temperature, it was acidified to Congo red and extracted with ether to remove the unchanged product. The aqueous layer was heated with HCl (conc., 30 c.c.) and sodium sulphite for 30 minutes, cooled, and extracted with ether. The ethereal solution furnished a solid (0.6 g.), which crystallised from ether-petroleum ether as pale yellow plates tapering at the ends; m.p. 133-34°; λ_{max} 240, 280, and 353 mμ (log ε, 4.16, 4.11, and 3.94 respectively); λ_{min} 237, 258, and 315 mμ (log ε, 4.15, 3.65, and 3.39 respectively). (Found: C, 65.7; H, 5.5. $C_{16}H_{16}O_5$ requires C, 66.6; H, 5.6%). It develops a green colour with ethanolic ferric chloride.

2-Hydroxy-4, 5-dimethoxyphenyl-4-methoxybenzyl Ketone (III).—(*a*). The above ketone (II) (1.44 g.), dimethyl sulphate (0.5 c.c.), and dry potassium carbonate (2.5 g.) were refluxed in acetone medium for 4 hours. Acetone was distilled off and the residue treated with water (50 c.c.). The insoluble solid crystallised from ethanol as colorless plates (1.2 g.), m.p. 99-100°; bluish green ferric reaction; λ_{max}^{EtOH} 280 and 345 mμ (log ε, 4.15 and 3.97 respectively); λ_{min}^{EtOH} 255 and 305 mμ (log ε, 3.65 and 3.49 respectively). (Found: C, 67.1; H, 6.5. $C_{17}H_{18}O_5$ requires C, 67.5; H, 6.0%).

(*b*). An ethereal solution of 1, 2, 4-trimethoxybenzene (IV) (8.5 g./50 c.c.) was added in one lot to an ice-cold ethereal solution of anhydrous aluminium chloride (27.2 g./400 c.c.) and it was followed by dropwise addition of *p*-methoxyphenylacetyl chloride (9.5 g.) during 2 hours. After leaving for 24 hours at room temperature, ether was distilled and the residual deep green complex decomposed by keeping it in contact with ice (200 g.) and HCl (conc., 135 c.c.) for 2 hours. The clear liquid was decanted and the semi-solid mass was macerated with a small amount of ether, when a colorless solid separated. It crystallised from ether-petroleum ether as colorless plates, m.p. 99-100°, alone or when mixed with the above sample.

6, 7, 4′-Trimethoxyisoflavone (VI).—A solution of the above deoxybenzoin (III) (4.5 g.) in freshly distilled ethyl formate (350 c.c.) was added slowly to pulverised sodium (3.7 g.) while the resulting mixture was cooled in ice, and shaken. After leaving for 48 hours at room temperature, ice was added to decompose the unchanged sodium, and the whole mixture was extracted with ether. The ethereal solution was washed with 2% aqueous NaOH, followed by water, dried, and concentrated when a colorless solid (2.5. g.) was left behind. It crystallised from ethanol as colorless, tiny prisms and melted at 142°, resolidified and remelted at 172-73°, and seemed to consist of 6, 7, 4′-trimethoxy-2-hydroxyisoflavanone (V). [Found (air-dried): C, 63.7; H, 6.3. $C_{18}H_{19}O_6$, $\frac{1}{2}$ H_2O requires C, 63.7; H, 5.6%).

The above solid was refluxed with acetic anhydride for 1 hour, cooled and poured into ice. The colorless solid, thus obtained, crystallised from ethanol as colorless plates, m.p. 174-75°; λ_{max} 260 and 318 mμ (log ε, 4.60 and 4.19 respectively); λ_{min} 235 and 297 mμ (log ε, 4.41 and 4.03 respectively). It showed no ferric reaction. McMurry and Theng (*loc. cit.*) also report the same properties.

6,7,4′-Trihydroxyisoflavone (VII).—The above isoflavone (VI) (2 g.), dry aluminium chloride (10 g.) and benzene (240 c.c.) were refluxed for 10 hours; benzene was distilled under vacuum and the residue treated with ice (50 g.) and HCl (conc., 50 c.c.). After leaving the mixture overnight, a colorless solid (0.7 g.) was obtained. It crystallised from methanol as colorless needles, m.p. 320-22° (decomp.) (lit., m.p. 322°, decomp.); λ_{max} 260 and 325 mμ (log ε, 4.45 and 4.06

respectively); λ_{min} 335 and 298 mμ (log ε, 4.29 and 3.91 respectively). It gave a green colour with ethanolic ferric chloride.

6,4'-Dihydroxy-7-benzyloxyisoflavone (VIII).—An acetone solution of the above isoflavone (0.7 g.) was refluxed with benzyl chloride (0.3c.c.), dry sodium iodide (1.5 g.), and ignited potassium carbonate for 5 hours. The inorganic salts were filtered, the acetone solution was concentrated to 10 c.c., and diluted with water (20 c.c.). After leaving it overnight, a colorless solid separated. It was collected and crystallised from ethyl acetate-petroleum ether (60-80°) when the 7-benzyl ether of the isoflavone (0.45 g.) was obtained as colorless, narrow, rectangular plates, m.p. 231-33°; λ_{max} 262 and 328 mμ (log ε, 4.47 and 4.06 respectively); λ_{min} 237 and 300 mμ (log ε, 4.27 and 3.88 respectively). (Found: C, 73.1; H, 5.3. $C_{22}H_{16}O_5$ requires C, 73.3; H, 4.4%). It gave a negative ferric reaction.

6,4'-Dimethoxy-7-benzyloxyisoflavone (IX).—The above benzyloxyisoflavone (VIII) (360 mg.) was refluxed with dimethyl sulphate (0.22 c.c.) and freshly ignited potassium carbonate (1 g.) in dry acetone solution (50 c.c.) for 12 hours. After removal of acetone, water was added to the residue when a colorless solid (350 mg.) was obtained. It crystallised from ethyl acetate as colorless, rectangular plates and needles, m.p. 150-51°; λ_{max} 260 and 318 mμ (log ε, 4.37 and 3.95 respectively); λ_{min} 237 and 297 mμ (log ε, 4.16 and 3.75 respectively). (Found: C, 74.5; H, 5.6. $C_{24}H_{20}O_5$ requires C, 74.2; H, 5.2%).

Afromosin (6, 4'-*Dimethoxy-7-hydroxyisoflavone*) (X).—The above isoflavone (IX) (150 mg.), acetic acid (8.5 c.c.), and HCl (conc., 5 c.c.) were heated on a boiling water bath for 2 hours. Acetic acid was partially distilled off under vacuum and the residue treated with water. A white solid separating was collected and it crystallised from ethanol as colorless needles, m.p. 228-29°; yield 75 mg., λ_{max}^{EtOH} 255 and 325 mμ (log ε, 4.41 and 4.04 respectively); λ_{min}^{EtOH} 237 and 295 mμ (log ε, 4.28 and 3.88 respectively). I R in KBr: 3.18 (O—H), 6.20 (pyrone C=O), 6.43 and 6.68 (aromatic C=C), 7.9 (aromatic C—O), and 9.62 μ (O—Me). In all these properties it agrees with the description of McMurry and Theng (*loc. cit.*) for the natural sample.

Methylation of Afromosin (X) *with Methyl Iodide.*—Afromosin (X) (100 mg.) was refluxed with methyl iodide (2 c.c.) and anhydrous potassium carbonate (2 g.) in dry acetone (20 c.c.) for 12 hours. The product was worked up as usual and it crystallised from ethanol as colorless plates (95 mg.), m.p. 174-75° alone or when mixed with a synthetic sample of 7-*O*-methylafromosin (VI), reported earlier. The UV spectrum also agreed.

Methylation of 6,7-Dihydroxyisoflavone with Methyl Iodide.—6, 7-Dimethoxyisoflavone was prepared by the method of Ballio and Pocchiari (*Gazzetta*, 1949, **79**, 913) and demethylated with aluminium chloride and benzene. The 6,7-dihydroxyisoflavone (0.180 g.) obtained was methylated with methyl iodide as described in the case of afromosin, when the product (0.150 g.) was found to be identical with 6,7-dimethoxyisoflavone, m.p. 170-71°.

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Received January 7, 1961.

[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

Behaviour of Sodium Diethyldithiocarbamate in Non-aqueous Solvents

K. P. Soni and A. M. Trivedi

Sodium diethyldithiocarbamate is a diacidic base. The two groups of the substance can be differentiated by titrating it in (*i*) acetic anhydride and (*ii*) acetic acid as solvents. The titration of the substance in (*i*) reveals the first break while that in (*ii*) reveals an overall jump, corresponding to the utilisation of two equivalents of $HClO_4$ in *p*-dioxane. This procedure can be applied for the estimation of the substance.

It has been shown previously (this *Journal*, 1960, **37**, 349) that sodium diethyldithiocarbamate is a diacidic base in water, the two dissociation constants of the corresponding acid being $pk_1 = 7.5$ and $pk_2 = 8.4$. In the present investigation the behaviour of sodium diethyldithiocarbamate in non-aqueous solvents has been studied. It has now been found that with acetic anhydride as a solvent, it is possible to obtain the first jump clearly while the second jump alone is obtained in solvents like acetic acid, ethanol, etc.

EXPERIMENTAL

A known quantity of sodium diethyldithiocarbamate (B.D.H., A.R.) was dissolved either in different solvents or their mixture and titrated against $HClO_4$ in acetic acid or *p*-dioxane. Chemicals used were either of B.D.H., A.R. or of Reagent grade. As the commercial *p*-dioxane gave a faint blue colour with $HClO_4$, *p*-dioxane of A.R., B.D.H. quality was used. Acetic anhydride was distilled before use.

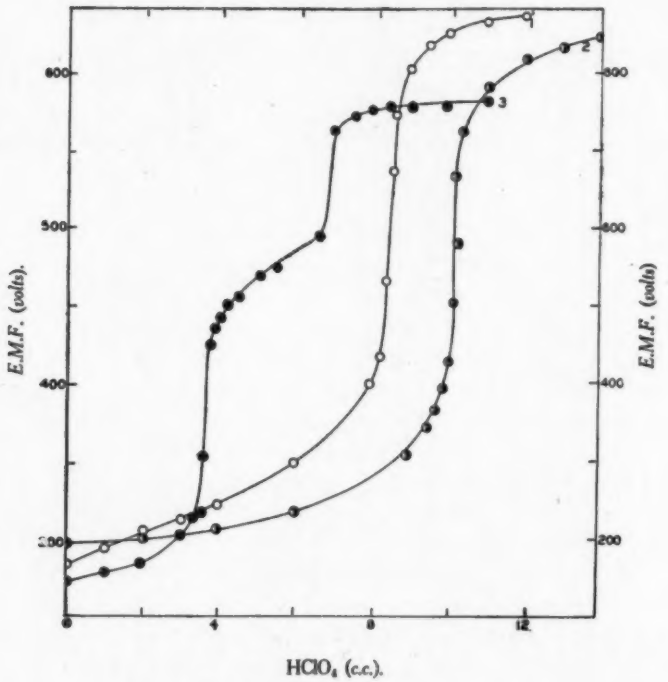
The end point of the reaction was detected potentiometrically using pH meter equipped with glass and calomel electrodes. $HClO_4$ in *p*-dioxane or acetic acid was standardised by titrating it against a weighed quantity of sodium bicarbonate in glacial acetic acid.

DISCUSSION

Curves 1 and 2 (Fig. 1) show the nature of the curve when 0.10 g. of the substance was dissolved in 25 c.c. of acetic acid and titrated against 0.104*N*-$HClO_4$ in acetic acid and 0.0882*N*-$HClO_4$ in *p*-dioxane respectively. A clear jump is observed at the utilisation of two equivalents of the titrant acid, showing diacidity of the substance. This is in agreement with our previous findings (*loc. cit.*). The neutralisation of the substance at two equivalents was found to be independent of concentration of the substance or of the solvent. The neutralisation at two equivalents was also observed when ethanol and nitrobenzene were used as solvents. In case of nitrobenzene, it is necessary to add a little acetic acid to dissolve the substance.

The mixed solvents are sometimes better than a single solvent as the colour changes of the indicators or potentiometric breaks are sharpened. Fig. 2 apparently shows that the end point is sharpened as the dielectric constant of the medium is decreased (Pifer and Wollish, *Anal. Chem.*, 1952, **24,** 300). Thus a mixture of *p*-dioxane-acetic acid (curve 3) is better than a mixture of chloroform-acetic acid (curve 2), which is better than acetic acid (curve 1). It is not possible, however, to use dioxane alone as a solvent as too low a dielectric constant results in unsteady potentials. Chloroform being an aprotic solvent tends to depress solvolysis and provides fairly sharp end points (Pifer *et al.*, *ibid.*, 1953, **25,** 310).

FIG. 1

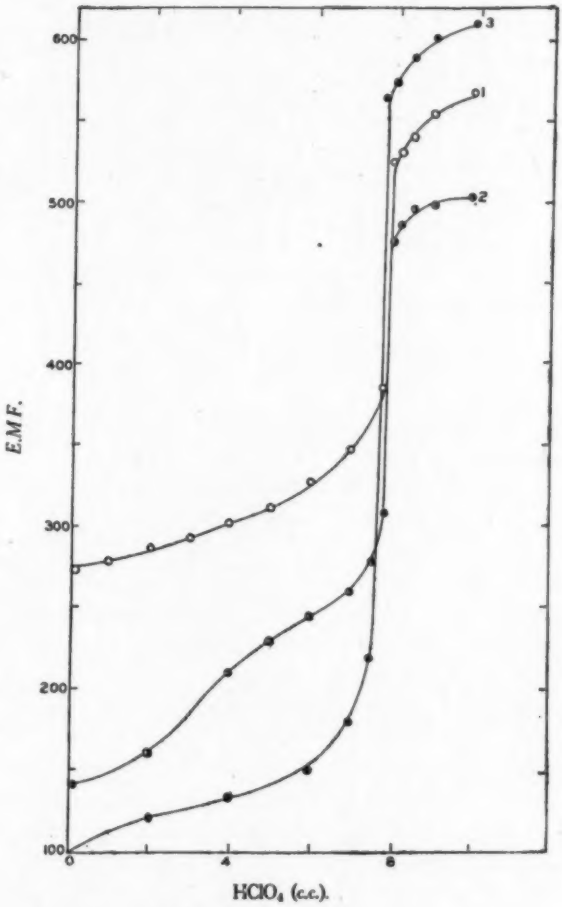


Curve No.	Scale axis. X.	Y.	Reagent.	AcOH.	Ac_2O.	$CHCl_3$.	Titrant. ($HClO_4$).	End point. Clac. I.	Clac. II.	Obs. I.	Obs. II.
1.	2 c.c.	50mv	0.1 g.	25c.c.	..	..	0.1044*N* in AcOH	..	8.5	..	8.5
2.	2	50	0.1	25	..	..	0.0882*N* in *p*-dioxane	..	10.07	..	10.1
3.	2	100	0.1	...	5c.c.	50c.c.	0·116*N* in *p*-dioxane	3.85	7.7	3.8	6.8

In the present investigation, we tried to differentiate the two basic groups of the substance. Acetonitrile was found the best to differentiate amines having pk's nearer to each other (Fritz, *ibid.*, 1953, **25,** 407). It was inapplicable in the present case, as the substance was found insoluble in acetonitrile. Intitrating certain weak amines, the water should be removed as much as possible by

titrating in a mixture containing acetic anhydride (Fritz and Fulda, *ibid.*, 1953, **25,** 1837). When the above procedure was applied to the present case, it was found that the first neutralisation jump at the utilisation of one equivalent of the acid was clear.

FIG. 2



Curve No.	Scale axis. X.	Y.	Reagent.	AcOH	*p*-Dioxane.	$CHCl_3$.	Titrant. ($HClO_4$).	End point. Calc. I.	II.	Obs. I.	II.
1.	2 c.c.	50mv	0.1 g.	55c.c.	..	..	0.113 *N* in *p*-dioxane.	..	7.9	..	7.9
2.	2	50	0.1	5	..	50c.c.	,,	..	7.9	..	7.9
3.	2	50	0.1	5	50c.c.	..	,,	..	7.9	..	7.8

Table I records the results of several experiments in different solvents. Table I shows that the first break at one equivalent is obtained in all the cases when acetic anhydride is used as a component of the solvent mixture; but the serious disadvantage of this solvent is the shifting of the second jump (see No. 1 to 6, 8 and 9).

TABLE I

In all experiments 0.10 g. of sodium diethyldithiocarbamate was taken.

No.	AcOH.	Ac_2O.	$CHCl_3$.	Aceto-nitrile.	Nitro-benzene.	Titrant $HClO_4$ in dioxane.	End points. Calc. I.	Calc. II.	Obs. I.	Obs. II.
1.	..	50 c.c.	..	..	..	0.113*N*	3.95	7.9	4.0	7.2
2.	..	10	100 c.c.	..	..	0.110	4.05	8.1	4.05	7.6
3.	*10 c.c.	10	100	..	..	0.110	4.05	8.1	4.0	7.7
4.	..	5	50	..	..	0.116	3.85	7.7	3.80	6.8
5.	5	5	100	..	..	0.088	5.04	10.08	5.0	8.5
6.	..	5	..	..	50 c.c.	0.116	3.85	7.7	3.8	6.9
7.	5	..	..	..	50	0.116	3.85	7.7	..	7.8
8.	..	10	..	20 c.c.	..	0.104	4.25	8.5	4.3	7.5
9.	..	5	50	20	..	0.104	4.25	8.5	4.25	9.0
10.	5	..	50	20	..	0.110	4.02	8.05	..	8.0

* Acetic acid (10 c.c.) added after first neutralisation.

The addition of acetic anhydride increases the dielectric constant of the medium; it also removes water from the system, thereby sharpening the end point. Mere shifting of the dielectric constant of the medium is not enough to obtain the first jump, as titrations carried out with mixtures (of different solvents) having nearly the same dielectric constant did not provide the first jump although the second or overall jump was observed. On the other hand, in the presence of acetic anhydride the second jump is shifted, which may be partly due to the change in dielectric constant of the medium and partly to the possibility of acetylation of the secondary amine, which may have been formed in the reaction.

In acetic acid medium the substance consumes exactly two equivalents of the acid and in presence of acetic anhydride, the first jump is exactly at the utilisation of one equivalent of the acid. Application of this procedure can differentiate the two groups.

Estimation of the Substance.—Dithiocarbamates may be estimated by direct titration with a standard iodine solution (Lieber *et al.*, *Ind. Eng. Chem. Anal. Ed.*, 1932, **4**, 98); alternatively gravimetric estimation of sulphur has been suggested (Linch, *Anal. Chem.*, 1951, **23**, 293). Both the methods are, however, liable to errors.

The present work suggests a neat method of estimating the substance by titrating it (dissolved in acetic acid) against perchloric acid in *p*-dioxane, when both the groups are estimated. On the other hand, using adequate proportion of acetic anhydride as one of the components of the solvent mixture, the first group is estimated. Thus estimation may be checked by two independent methods. The presence of basic impurities will interfere with the estimation. The fact that the titre value for the overall jump is double the titre value of the first jump, indicates that such impurities may not be present.

Thanks are due to Mr. I. M. Bhatt for checking some of the analytical data. Thanks are also due to the Ahmedabad Education Society and the Gujarat University for a grant towards chemicals and apparatus.

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Received October 18, 1960.

[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

Studies on Stability and Electrokinetic Potential of Sulphur Hydrosol

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A fairly pure and stable sulphur hydrosol has been prepared by a slight modification of von Janek's method with a view to ascertaining the existence of any relation between stability and electrokinetic potential. The true zeta-potential of the sol found for rapid coagulation from electro-osmotic data is 31.3 mv, while that found for slow coagulation both by electro-osmotic and electrophoretic methods is 38.4 mv.

A correction for surface conductance, which is quite marked in this case, has been applied by using an equation of the form :

$$\frac{1}{\zeta_a} = \frac{1}{\zeta} + m\frac{1}{S} .$$

A given rate of coagulation of the sol is characterised by a definite value of the true zeta-potential, independent of the valency of the counter ions used.

Attempts were made in the past to correlate the stability of a colloid with its electrical charge or the potential of the electrical double layer. Experimental results of Powis (*J. Chem. Soc.*, 1916, **109,** 734), Mukherjee *et al.* (this *Journal*, 1928, **5,** 735), Kruyt *et al.* (*Z. physikal. Chem.*, 1927, **130,** 170), and Ghosh (*J. Chem. Soc.*, 1929, 2693) on As_2S_3 sol, and also of Kruyt *et al.* (*Kolloid Z.*, 1937, **78,** 32) and Weiser *et al.* (*J. Phys. Chem.*, 1938, **42,** 119) on AgI and other sols do not support either Hardy's theory (*Proc. Roy. Soc.*, 1900 **A66,** 110) of coagulation at the isoelectric point or Powis' theory (*Z. physikal. Chem.*, 1915, **89,** 186) of coagulation at a critical potential. According to Hermans (*Trans. Faraday Soc.*, 1940, **36,** 133), Verwey and Overbeek ("Theory of the Stability of Lyophobic Colloids", 1948), Rutgers (*Trans. Faraday Soc.*, 1940, **36,** 69), Bikerman (*ibid.*, 1940, **36,** 154) and others an error of the order of 100% or more may occur in calculating the zeta-potential by the Smoluchowski equation (*Z. physikal. Chem.*, 1918, **93,** 129).

Rutgers (*loc. cit.*) has shown that the true zeta-potential (ζ) of a uniform glass capillary wall of radius 'r' in contact with a very dilute electrolyte solution or in water can be determined by the following formula :

$$\zeta = \frac{4\pi\eta}{D} . S . \frac{E_1}{P}\left(1 + \frac{2\chi}{rS}\right) = \zeta_1\left(1 + \frac{2\chi}{rS}\right) \qquad .. \quad (1)$$

where E_1 = streaming potential, P = the pressure used for streaming the liquid through the capillary, χ = the specific surface conductance, and S = the specific conductance of the liquid in bulk.

Overbeek and Wijga (*Rec. trav. chim.*, 1946, **65,** 556) have shown that equation (1) holds for a single glass capillary, but fails in the case of a porous diaphragm made of powdered glass particles.

Ghosh (this *Journal*, 1954, **31,** 274, 393) has shown from Wijga's data on streaming potential of powdered pyrex and Jena glass diaphragms that the true zeta-potential can be calculated from the equation :

$$\zeta = \zeta_a\left(1 + \frac{2\alpha\chi}{Sr}\right) \qquad .. \quad (2)$$

where α is a correction factor for the diaphragm.

Recently, Ghosh (*Trans. Faraday Soc.*, 1953, **49,** 1977) has deduced the following expression for the true zeta-potential of the particles of As_2S_3 sol in the form of a diaphragm, which has been further verified by Ghosh and Rakshit (*Science & Culture*, 1953, **18,** 498) and others on a number of different colloids :

$$\zeta/\zeta_a = 1 + \frac{3\chi}{aR} \cdot \frac{1}{S} \quad \ldots \quad (3)$$

where R = radius of the spherical particles forming the diaphragm, a = the ratio of the volume V_2 of liquid to the volume V_1 of solid in the diaphragm, χ = the specific surface conductance, S = the bulk conductance of the supernatant solution, and ζ_a = the apparent ζ-potential calculated by using Smoluchowski's equation from electro-osmotic data.

Ghosh has further shown that equation (3) can be expressed in the following form :

$$\zeta/\zeta_a = 1 + \frac{3r}{2aR}\left(\frac{2\chi}{rS}\right) = 1 + \frac{3\,V_1\,r}{2\,V_2\,R}\left(\frac{2\chi}{rS}\right) \quad \ldots \quad (3a)$$

or
$$\zeta/\zeta_a = 1 + \alpha\left(\frac{2\chi}{rS}\right) \quad \ldots \quad (3b)$$

or
$$\frac{1}{\zeta_a} = \frac{1}{\zeta} + m.\frac{1}{S} \quad \ldots \quad (4)$$

where $\alpha = 3r/2aR$ and r is the average radius of a typical pore in the diaphragm, and $m = (2\alpha\chi)/r\zeta$.

For electrophoresis, when (Ka) is large (K is the reciprocal of the thickness of the double layer and a is the radius of the particles), Ghosh *et al.* (*Nature*, 1955, **176,** 1081) have shown that the expressions of Booth (*Trans. Faraday Soc.*, 1948, **44,** 455) and Henry (*ibid.*, 1948, **44,** 1021) reduce to the form :

$$\frac{1}{\zeta_a} = \frac{1}{\zeta} + m^1.\frac{1}{S} \quad \ldots \quad (5)$$

where $m^1 = \chi/R\zeta$. They have also shown for a number of sols that corresponding to a given rate of coagulation by electrolytes, there is a definite value of true zeta-potential, independent of the valency of the counter ions used.

A systematic investigation has been undertaken to ascertain if a similar relation between true zeta-potential and rate of coagulation also holds in the case of sulphur hydrosol.

EXPERIMENTAL

Among the various methods of preparing hydrosol of sulphur the present authors tried those of Odén (*Z. Chem. Ind. Koll.*, 1911, **8,** 186), Ostwald and Egger (*Kolloid Z.*, 1927, **43,** 353), and von Weimarn and Malyschew (*ibid.*, 1911, **8,** 216), but could not obtain a fairly stable and concentrated sol. A slight modification of von Janek's method (*ibid.*, 1933, **64,** 31), however, furnished a hydrosol of the desired quality.

Preparation of the Sol

The standard solutions used for preparation of the sulphur hydrosol were : (*a*) 72 g./litre of Na_2SO_3 solution ; (*b*) 128 g./litre of $Na_2S,9H_2O$ solution ; (*c*) 270 g./litre of H_2SO_4 (*d* 1.84) ; (*d*) H_2SO_4 (*d* 1.84). All solutions were prepared from E. Merck's guaranteed reagent.

To 1000 c.c. of solution (*b*), taken in a 2-litre pyrex flask and cooled in a bath of ice-cold water, 30 c.c. of solution (*a*) was added. To 970 c.c. of solution of (*a*), taken in a 4-litre pyrex flask, also cooled in a bath of ice-cold water, about 60 c.c. of H_2SO_4 (conc.) was added in small instalments with constant stirring. About 160 c.c. of solution (*c*) was then added dropwise to the mixture of $Na_2S-Na_2SO_3$ solution with frequent stirring till a permanent turbidity just appeared. This solution was then poured into the mixture of $Na_2SO_3-H_2SO_4$ and shaken vigorously, when an opaque, yellowish white sol was formed. It was allowed to stand for 1 hour in an ice-cold water bath when most of the sulphur particles separated at the bottom. The solution was filtered through a fluted filter paper, the residue washed, and finally peptised with conductivity water (about 1,000 c.c.). The sol thus formed was dialysed for 7 days in cellophane bags against conductivity water. About 6 litres of the sol was thus prepared and allowed to age for 15 days. In this period the bigger particles settled to the bottom and the middle portion was siphoned off and collected in another Jena flask. The sol thus prepared was negatively charged and moderately stable; its *p*H was 4.45.

Equicoagulating Concentration of Electrolytes

The concentrations of different electrolytes, which coagulated a colloid at a given rate, have been termed as the equicoagulating concentrations.

The electrolytes used for coagulation were: NaCl, $MgCl_2$, $AlCl_3$, mixture of NaCl + $MgCl_2$, NaCl + $AlCl_3$. Four pairs of clean and dry test tubes of equal size were arranged in two rows (4 in each row) in a stand. The test tubes were marked from '1' to '4' (in one of the row). Into each of the marked test tubes different amounts (2c.c. or less) of an electrolyte of a definite strength were added and the volume in each test tube was made to 2 c.c. by addition of conductivity water (where necessary). Two c.c. of the sol was taken into each of the test tubes kept in the other row. Finally, the electrolyte in the test tube marked '1' was poured into the opposite test tube containing the sulphur sol. The sol-electrolyte mixture was poured back to the test tube marked '1', which was corked and allowed to stand for 30 minutes. In the same way, the electrolytes taken in the other test tubes were mixed with the sol and allowed to stand for 30 minutes. As there was no sharp separation of a clear meniscus, the sol-electrolyte mixture was centrifuged for 2 minutes at a definite speed after allowing it to stand for 30 minutes. The supernatant solution was examined for transparency for determining the equicoagulating concentration of the electrolyte. A large number of experiments was performed for determining accurately the equicoagulating concentrations with different electrolytes.

The same method was followed for determining the equicoagulating concentrations of electrolytes when the rate of coagulation was slow, *i.e.*, boundary separation occurred after 24 hours.

Electro-osmotic Experiments

A definite volume (200 c.c.) of the sol was taken in a clean and dry Jena bottle (500 c.c. capacity) and to it was added an equal volume of an electrolyte of requisite strength; the mixture was allowed to stand for 30 mins. and 24 hrs. for the rapid and slow rates of coagulation respectively. The coagula separating from the supernatant liquid after centrifuging were transferred into a 'U' tube, which was then centrifuged at a definite speed whereby a compact diaphragm was formed. The electro-osmotic velocity was measured by the moving bubble method of Mukherjee *et al* (this *Journal*, 1927, **4**, 493).

The experiments were performed at 25°. The distance between the two electrodes and the mass of coagula, and the volume it occupied in the U-tube were kept constant. To minimise resistance

to the flow of liquid, the side tubes and the stopcocks were so selected as to have sufficiently wide bore; the length of the air bubble in the horizontal tube was about 0.4 cm. These precautions were necessary for maintaining some of the variable factors constant.

The extrapolated values of the true zeta-potential of sulphur hydrosol in the regions of rapid and slow rates of coagulation were found to be 31.3 mv and 38.4 mv.

TABLE I

Electro-osmosis of sulphur hydrosol (rapid coagulation).

Time for coagulation = 30 minutes. Temp. = 25°.

$1/\zeta = 0.032$ mv. $\zeta = 31.3$ mv. $m = \frac{2\pi\chi}{\zeta r} = 6.287 \times 10^{-5}$.

Electrolyte used.	Equicoag. conc.	Supernatant solution. pH.	Supernatant solution. S (mhos cm.$^{-1}$) $\times 10^4$.	Calculated values of ζ_a from Smoluchowski's eq.*	Calculated values of ζ_a from eq. (4)**
NaCl	$5.54\times10^{-1}N$	3.50	515.50	30.3 mv	30.1 mv
NaCl & $MgCl_2$	4.08×10^{-3} & 6.59×10^{-3}	3.62	13.96	12.8	13.0
$MgCl_2$	6.59×10^{-3}	3.52	9.00	8.0	9.3
NaCl & $AlCl_3$	1.63×10^{-2} & 1.60×10^{-3}	3.70	11.12	11.2	11.3
NaCl & $AlCl_3$	1.30×10^{-2} & 1.62×10^{-3}	3.70	4.81	6.2	6.2
$AlCl_3$	1.65×10^{-3}	3.62	3.58	4.9	4.8

* From electro-osmotic data.

** Using the values of ζ and m.

TABLE II

Electro-osmotic data of sulphur hydrosol at 25° (slow coagulation).

$1/\zeta = 0.026$. $\zeta = 38.4$ mv. $m = \frac{2\pi\chi}{\zeta r} = 4.814 \times 10^{-5}$.

Electrolyte used.	Equicoag. conc.	Supernatant solution. pH.	Supernatant solution. S (mhos cm^{-1}) $\times 10^4$.	Calculated values of ζ_a from Smoluchowski's eq.*	Calculated values of ζ_a from eq. (2)**
NaCl	$1.87\times10^{-1}N$	3.55	189.90	34.4 mv	35.0 mv
NaCl & $MgCl_2$	4.89×10^{-3} & 4.26×10^{-3}	3.60	12.14	15.4	15.2
NaCl & $MgCl_2$	1.63×10^{-2} & 4.18×10^{-3}	3.60	8.34	12.1	12.0
$MgCl_2$	4.00×10^{-3}	3.60	6.57	10.2	10.1
$AlCl_3$	1.39×10^{-3}	3.60	3.33	5.8	5.8

* From electro-osmotic data.

** Using the values of ζ and m.

In the rapid and slow rates of coagulation, the *p*H of the supernatant solutions with different electrolytes remained within 3.50 to 3.70 and 3.55 to 3.60 respectively. Tables I and II show that the effect of surface conductance is appreciable. The values of the apparent zeta-potential varied from 4.9 to 30.3 mv and 5.8 to 34.4 mv for rapid and slow rates respectively.

Electrophoretic Experiments

These experiments were carried out at 25° in a modified form of Burton's U-tube apparatus (Ghosh *et al.*, *loc. cit.*, p. 1081). Reversible Ag, AgCl electrodes were used and the electrolytes selected contained Cl^- as anion.

Preparation of the Colloid-electrolyte Mixture.—The sulphur hydrosol (40 c.c.) was mixed with the electrolyte (40 c.c.) of desired strength; the mixture was allowed to stand for 28 minutes and then centrifuged for 2 minutes at a definite speed. The big particles settled at the bottom; the rest of the colloid-electrolyte mixture was decanted and used for filling the lower part and funnel of the U-tube.

Preparation of the Supernatant Liquid.—The sol (200 c.c.) was mixed with the electrolyte (200 c.c.) of desired strength in a Jena bottle and allowed to stand for 24 hours. The mixture was centrifuged for 3 minutes at a definite speed to furnish a clear supernatant liquid, which was stored in a Jena bottle and used for filling the upper part of the U-tube and the electrode vessels communicating with the limbs of the U-tube through ground-glass joints. The coagula, which remained in the centrifuging tubes, were used for preparation of the diaphragm required for electro-osmotic experiments.

The distance moved by the colloid boundary under a given current in a given time was measured. The mean value of the upward and downward movement of the boundary was taken for calculation of ζ_a by Smoluchowski's equation. The results are recorded in Table III.

TABLE III

Electrophoresis of sulphur hydrosol (slow coagulation).

Time for coagulation = 24 hours. Temp. = 25°.

$1/\zeta = 0.026$ mv. $\zeta = 38.4$ mv. $m^1 = \frac{\chi}{\zeta r} = 1.885 \times 10^{-5}$.

Electrolyte used.	Equicoag. conc.	S_1 of supernat. soln. (mhos cm^{-1}).	S_2 of sol-electrolyte mixture (mhos cm^{-1}).	Calculated values of ζ_a from Electrophoretic data using Smoluchowski's eq.	eq. (3) using the value of ζ and m^1.
NaCl	$1.87\times10^{-1}N$	185.23×10^{-4}	192.09×10^{-4}	36.5 mv	37.0 mv
NaCl & $MgCl_2$	4.89×10^{-2} & 4.26×10^{-3}	12.58	12.41	24.0	24.3
NaCl & $MgCl_2$	1.63×10^{-2} & 4.18×10^{-3}	8.45	8.48	21.0	20.8
$MgCl_2$	4.00×10^{-3}	6.46	6.52	18.0	18.2

DISCUSSION

It is noticed from columns (3) of Tables I and II that the *p*H's of the supernatant solutions with different electrolytes for rapid and slow rates of coagulation remain within 3.50 to 3.70 and 3.55 to 3.60 respectively.

From the data recorded in columns (4) and (5) of Tables I and II and columns (3), (4), and (5) of Table III, the values of $1/S$ and $1/\zeta_a$ have been calculated ; when these are plotted a straight line is obtained in every case. The value of m has been found from the slope of the straight line and the true ζ from the intercept of the straight line on the $1/\zeta_a$ axis.

It appears from Table I that the effect of surface conductance is appreciable. The values of ζ_a for rapid rate of coagulation for different electrolytes varied from 4.9 to 30.3 mv. The ζ_a values for different electrolytes are evaluated by means of equation (4) and are compared with ζ_a values obtained from electro-osmotic data using Smoluchowski's equation. It is evident from the data in columns (5) and (6), that the values of ζ_a found from electro-osmotic data using Smoluchowski's equation do not differ appreciably (except for $MgCl_2$) from the corresponding values calculated by means of equation (4).

Tables II and III evidently show that the effect of surface conductance is also appreciable both for electrophoretic and electro-osmotic methods in the region of slow coagulation, the effect in the latter method being more marked.

Again, the values of ζ_a for different electrolytes, calculated by equations (4) and (5) from electro-osmotic and electrophoretic data respectively for the slow rate of coagulation, agree well (cf. columns 5 and 6 in Tables II & III) with the corresponding ζ_a values, calculated from experimental data using the Smoluchowski equation.

The true zeta-potential (ζ), calculated both from electro-osmotic and electrophoretic data, is 38.4 mv for the slow rate of coagulation while that found for rapid rate of coagulation is 31.3 mv.

The true zeta-potential of sulphur hydrosol depends therefore on the rate of coagulation, the more rapid the rate, the smaller it is in magnitude.

In conclusion it may be pointed out, that a fairly pure sulphur hydrosol possesses an appreciable surface conductance.

The authors express their grateful thanks to the C. S. I. R. for a research grant.

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Received November 28, 1960.

[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

Dimethylaminohydroxyphenoxazone Carboxylic Acid as an Indicator in Complexometric Determination of Thorium

Satendra Prashad Sangal and Arun K. Dey

Use of dimethylaminohydroxyphenoxazone carboxylic acid (gallocyanine) as an indicator in the complexometric determination of thorium with EDTA has been described. The use of 0.03 c.c. of indicator solution (0.02% in 5% Na_2CO_3 and neutralised to *p*H 7.0) in each titration has been recommended. Sharp end points are observed up to a dilution of 0.0033*M* thorium chloride. The titrations are possible in the temperature range of 0°-100°, but *p*H must be adjusted between 2.0 and 2.7. Several added foreign ions are found to interfere, but there is no interference from lithium, sodium, potassium, silver, calcium, strontium, barium, zinc, mercury, lead, and manganese ions.

Dimethylaminohydroxyphenoxazone carboxylic acid (gallocyanine) has found application in the detection of lead (Poole, B.D.H. Book of Spot Tests). Pavelka (*Mikrochem.*, 1930, **2,** 345) reported characteristic colour reactions with several metals including thorium. Pavelka and Heisnar (*Kolloid Z.*, 1934, **66,** 340) also observed that the lakes with metals did not form definite stoichiometric compounds. Work in progress in these laboratories shows that gallocyanine forms coloured chelates with several metals and that the thorium chelate is violet in colour with λ_{max} 545 mμ at *p*H 1.5.

Sangal and Dey (*Z. anal. Chem.*, 1961, in press) have reported the use of Chromeazurol S as a metal indicator in the complexometric determination of thorium. The present paper records our observations on gallocyanine as a suitable indicator for complexometric titrations of Th-EDTA.

EXPERIMENTAL

A solution of BDH-AnalaR grade thorium chloride was prepared and standardised by precipitating thorium as oxalate in a 4% solution of HCl. It was ignited at 800° and weighed as ThO_2. An exact solution of 0.1*M* was prepared by suitable dilution.

A 0.02% solution of gallocyanine was prepared by dissolving 0.1 g. of the dye (BDH spot test reagent) in a 5% aqueous solution of Na_2CO_3. The volume was made to 500 c.c. after adjusting the *p*H of the solution to 7.0.

A 0.1*M*-EDTA solution was prepared by dissolving 18.6126 g. of its disodium salt in 500 c.c. and the concentration was checked against a primary standard solution of calcium chloride according to Goetz *et al.* (*Anal. Chem.*, 1947, **19,** 222).

Foreign Ions.—0.1*M* solutions of the various reagents were prepared either by direct weighing or by standardising the solutions by the usual methods. Reagent grade chemicals were used.

A microburette with a least count of 0.02 c.c. was used for measuring the solutions. *p*H measurements were done by using a stabilised L & N *p*H indicator operated on 220V/50 cycles A.C. mains with a glass—calomel electrode system, supplied by the same manufacturer.

Concentration of the Indicator.—In the titration the end point may be detected by the change in colour from blue to pink when EDTA is added to the thorium chloride solution. The effect of concentration of the dye on the end point is of great importance, as with the change of its concentration the end point is slightly shifted. Accurate results with sharp end points are obtained by using 0.30 c.c. of the indicator solution for each titration.

Limit of Dilution.—Titrations were carried out with the solutions of different molarity and the titrations of thorium against EDTA were possible up to 0.0033*M* solutions ; on further dilution the end point was not very sharp.

Effects of Temperature and pH.—Temperature effect between 0° and 100° was negligible. Titrations were carried out at different pH values of the thorium chloride solution. It may be seen that the pH of thorium solution suitable for titration is 2.0 to 2.7 (Table I).

TABLE I

Effect of pH.

0.02*M*-EDTA required = 10 c.c. Thorium taken = 0.0464 g.

pH ..	1.4	1.6	2.0	2.35	2.7	2.9	3.0	3.3
EDTA (c.c.)	No sharp end point	10.06	10.02	10.00	10.00	9.40	9.00	No sharp end point

Procedure.—A known quantity of thorium chloride solution was taken in a 250 c.c. Erlenmeyer flask ; the pH of the solution was adjusted to 2.7 and 0.3 c.c. of indicator solution was added. The solution was now titrated against a standard EDTA solution with constant shaking until a distinct change of colour from blue to pink took place. Thorium present in the solution was determined from g. Th = $0.2321 \times V \times M$ (where V is the volume and M is the molarity of the EDTA solution).

In order to compare the results and examine the suitability of the indicator, titrations with known solutions were carried out. Typical results are shown in Table II.

TABLE II

Thorium	Taken (mg.) ..	0.0928	0.0348	0.0232	0.0580	0.0696	0.0464	0.0812
	Found (mg.) ..	0.0927	0.0347	0.0231	0.0580	0.0695	0.0464	0.0811
	Diff ..	-0.0001	-0.0001	-0.0001	Nil	-0.0001	Nil	-0.0001

Interference due to Foreign Ions.—Presence of foreign ions caused interferences in the titrations due to the formation of stable versene complexes by the cations present, or a coloured complex with the indicator, or precipitates in certain cases. For noting the interference, titrations were carried out using 5 c.c. of 0.02*M* thorium chloride in presence of equimolar amounts of various cations and anions directly against EDTA

The observation show (the detailed titre values have been omitted to economise space) that the following anions and cations interfere : tartrate, oxalate, acetate, citrate, tetraborate, phosphate, fluoride, Cu(II), Au (III), Be(II), Mg (II), Cd(II), Al(III), Ti (IV), Zr(IV), Sn (IV), V (V), As(III), Sb (III), Bi (III), Cr (VI), Mo(VI), W (VI), Fe (III and II), Co (II), Ni (II), Ce (IV), and uranyl (II). On the other hand, the alkali and alkaline earth metals, silver (I), zinc (II), Hg (II), Pb (II), and Mn (II) do not interfere. Further work on the elimination of interfering ions in these titrations is in progress.

The authors thank the Council of Scientific and Industrial Research for the grant of a research fellowship to one of them (S.P.S.).

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Received October 31, 1960.

[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

Synthesis of New Local Anaesthetics. Part IV*

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Diethylaminoacetyl-2-amino-, -4-methyl-, -5-methyl-, -6-methyl-, -6-chloro-, -6-methoxy-, and -6-ethoxy-benzothiazoles and their hydrochlorides have been synthesised and their local anaesthetic activity has been tested. The pharmacological screening has shown that the hydrochloride of diethylaminoacetyl-2-amino-6-chlorobenzothiazole is the most active of all the compounds described here and diethylaminoacetyl-2-amino-6-methylbenzothiazole is the most active amongst the three methyl derivatives.

Hugershoff (*Ber.*, 1903, **36,** 3121) prepared 2-aminobenzothiazoles by the action of liquid bromine on asymmetrical phenylthiourea in chloroform. Brewster and Dains (*J. Amer. Chem. Soc.*, 1936, **58,** 1364) prepared several thiazoles by the cupric thiocyanate method and found that thiocyanation did not occur in compounds containing acetamido or ethoxycarbonylamino groups. In continuation of the previous work on 2-aminobenzothiazoles by Bhargava *et al.* (this *Journal*, 1958, **35,** 807 ; 1960, **37,** 314), it was therefore considered worthwhile, in view of their medicinal importance as local anaesthetics, to prepare 2-aminobenzothiazole, 2-amino-4-methyl-, -5-methyl-, -6-methyl-, -6-chloro-, -6-methoxy-, and -6-ethoxy-benzothiazoles and to convert these respectively into diethylaminoacetyl-2-amino-, -4-methyl-, -5-methyl-, -6-methyl-, -6-chloro-, -6-methoxy-, and -6-ethoxy- benzothiazoles, firstly by condensation with chloroacetyl chloride and secondly with diethylamine. The hydrochlorides of these bases have been prepared and their local anaesthetic activity has been tested.

A study of the pharmacological screening shows that the hydrochloride of diethylaminoacetyl-2-amino-6-chlorobenzothiazole is the most active of these compounds, confirming thereby that a chlorine atom in *para* position in the benzene nucleus confers more activity on the compound than the presence of a higher aromatic nucleus (Bhargava *et al.*, *ibid.* 1960, **37,** 241). Further, it is proved that diethylaminoacetyl-2-amino-6-methylbenzothiazole is the most potent compound amongst the methyl derivatives prepared.

* Part III : This *Journal*, 1960, **37,** 314.

EXPERIMENTAL

2-Aminobenzothiazoles were prepared according to the procedure of Hugershoff (*loc. cit.*). Analytical data of the compounds are recorded in Table I.

TABLE I

*Compounds.	%Yield.	M.P.	Formula.	%Sulphur. Found.	Calc.
1. A-B	75	129°	$C_7H_6N_2S$	20.70	21.33
2. A-4-methyl-B	70	136°	$C_8H_8N_2S$	19.30	19.51
3. A-5-methyl-B	72	143°	$C_8H_8N_2S$	19.24	19.51
4. A-6-methyl-B	75	138°	$C_8H_8N_2S$	19.09	19.51
5. A-6-chloro-B	70	198°	$C_7H_5N_2ClS$	17.02	17.34
6. A-6-methoxy-B	69	146°	$C_8H_8ON_2S$	17.32	17.77
7. A-6-ethoxy-B	74	174°	$C_9H_{10}ON_2S$	16.06	16.49

* B denotes benzothiazole. A denotes 2-amino-.

Chloroacetyl-2-aminobenzothiazole.—Freshly distilled chloroacetyl chloride (3.0 c.c.), dissolved in pure benzene (10 c.c.), was gradually added to 2-aminobenzothiazole (5.0 g.), dissolved in benzene (35 c.c.). The reaction mixture was warmed at 70° on a water bath for 1½ hours. Benzene was distilled ; the residue was washed with sodium bicarbonate solution and water, and finally dried. The product was crystallised from ethanol, m.p. 156°, yield 4.8 g.

Chloroacetyl derivatives of other 2-aminobenzothiazoles were similarly prepared. Analytical data are recorded in Table II.

TABLE II

Compounds.	%Yield.	M.P.	Formula.	%Sulphur. Found.	Calc.
1. Chloroacetyl-A-B	60	156°	$C_9H_7ON_2ClS$	13.95	14.13
2. Chloroacetyl -A-4-methyl-B	70	180°	$C_{10}H_9ON_2ClS$	13.01	13.30
3. Chloroacetyl-A-5-methyl-B	82	185°	$C_{10}H_9ON_2ClS$	12.98	13.30
4. Chloroacetyl-A-6-methyl-B	75	183°	$C_{10}H_9ON_2ClS$	13.00	13.30
5. Chloroacetyl-A-6-chloro-B	68	202°	$C_9H_6ON_2Cl_2S$	12.02	12.26
6. Chloroacetyl-A-6-methoxy-B	70	155°	$C_{10}H_9O_2N_2ClS$	12.35	12.47
7. Chloroacetyl-A-6-ethoxy-B	72	166°	$C_{11}H_{11}O_2N_2ClS$	11.58	11.85

Diethylaminoacetyl-2-aminobenzothiazole.—To chloroacetyl-2-aminobenzothiazole (5 g.), dissolved in ethanol (50 c.c.), diethylamine (3.5 c.c.) was added ; the mixture was refluxed for 5 hours. After the reaction, excess of ethanol and diethylamine were recovered by distillation and

the residue was washed with sodium bicarbonate to remove the acid impurities, and finally with water. The product was crystallised from ethanol and recrystallised from benzene in grey form, m.p. 120°.

Diethylaminoacetyl derivatives of the other 2-aminobenzothiazoles were similarly prepared. Their hydrochlorides were also prepared as usual and crystallised from ethanol-ether mixture (1 : 1). Analytical data are recorded in Table III.

TABLE III

*Compounds.	Diethylaminoacetyl-2-aminobenzothiazole. M.P.	Formula.	%Sulphur. Found.	%Sulphur. Calc.	Hydrochlorides. M.P.	%Chlorine. Found.	%Chlorine. Calc.
1.	120°	$C_{13}H_{17}ON_3S$	11.98	12.16	166°	11.76	11.85
2.	160°	$C_{14}H_{19}ON_3S$	11.36	11.55	210°	11.00	11.32
3.	154°	$C_{14}H_{19}ON_3S$	11.62	11.55	200°	11.08	11.32
4.	145°	$C_{14}H_{19}ON_3S$	11.46	11.55	150°	11.48	11.32
5.	175°	$C_{13}H_{16}ON_3ClS$	10.78	10.75	220°	21.02	21.25
6.	185°	$C_{14}H_{19}O_3N_3S$	11.02	10.92	230°	10.68	10.77
7.	170°	$C_{15}H_{21}O_3N_3S$	10.56	10.42	235°	10.26	10.33

* The number corresponds to those in Table II.

Pharmacological Test : Plexus Anaesthesia in Frogs.—Hydrochloride solutions (0.1% and 0.2%) were used and the time of onset of anaesthesia was recorded and compared with that of procaine hydrochloride as a standard substance. The results are shown in Table IV.

TABLE IV

Hydrochloride of diethylaminoacetyl-	With 0.1% solution for onset of anaesthesia in 0.05*N*-HCl.	With 0.1% solution for onset of anaesthesia in 0.1*N*-HCl.	With 0.2% solution for onset of anaesthesia in 0.05*N*-HCl.	With 0.2% solution for onset of anaesthesia in 0.1*N*-HCl.
1. *Procaine hydrochloride	10 mins.	16 mins.	7 mins.	14 mins.
2. -A-B	19	22	16	19
3. -A-4-methyl-B	14	21	12	18
4. -A-5-methyl-B	12	17	10	15
5. -A-6-methyl-B	10	26	7	12
6. -A-6-chloro-B	6	8	4	6
7. -A-6-methoxy-B	12	18	11	16
8. -A-6-ethoxy-B	11	16	9	14

* It was used as such and not in the form of diethylamino derivative.

The study of pharmacological screening has shown that the hydrochloride of diethylamino-acetyl-2-amino-6-chlorobenzothiazole is the most active of all the compounds and diethylamino-acetyl-2-amino-6-methylbenzothiazole is the most potent amongst the three methyl-substituted derivatives described here.

Thanks are due to the authorities of the Banaras Hindu University for providing necessary facilities.

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Received November 25, 1960.

[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

Studies in Acetyl Bromide as a Polar Solvent. Part I. Solubility of Substances, Formation of Solvates, and Electrical Conductance of Solutions

Ram Chand Paul, Sarjit Singh Sandhu, and Jagtar Singh Bassi

Solubilities of several substances including a few Lewis acids, bromides, and organic tertiary bases have been tried in acetyl bromide and the formation of solvates in this solvent has been studied. Solutions of the Lewis acids and bases in acetyl bromide have been found conducting, which indicates the formation of ion pairs. The constitution of these solutions has been discussed.

The physical properties of acetyl bromide, *i.e.*, dielectric constant 16.5 at 20° (International Critical Tables, 1929, VI, p. 84), m.p. -96.5°, b.p. 76.7° (Handbook of Chemistry & Physics, Chemical Rubber Publishing Company, 39th ed., 1957-58, p. 725), electrical conductance 2×10^{-6} $ohm^{-1}\,cm^{-1}$ (International Critical Tables, 1929, VI, p. 143), and relatively long carbonyl-bromine bond 2.00 Å as compared to methyl bromide, 1.936 Å (Allen and Sutten, *Trans. Faraday Soc.*, 1951, **47**, 236), are suggestive of a slightly polar character of the solvent. The work, which is being reported in this and the subsequent parts, supports the auto-ionisation of acetyl bromide as :

$$CH_3COBr \rightleftharpoons CH_3\overset{+}{C}O + Br^-.$$

Solubility of the substances in this liquid reveals that, in general, only the covalent compounds are soluble while ionic compounds are insoluble ; this is expected of the solvents having a low dielectric constant. Solubility of the compounds has been studied quantitatively and in some cases qualitatively. The results are presented in Tables IA and IB. The Lewis acids and bases mostly dissolve to form coloured solutions in acetyl bromide, indicating formation of complexes in solution. Pyridine, β-picoline, γ-picoline, isoquinoline, and triethylamine are sparingly soluble and form solid solvates, which are discussed later on.

Literature records the formation of a monosolvate by *NN*-dimethylformamide with acetyl bromide (Hall, *J. Amer. Chem. Soc.*, 1956, **78**, 2717). Acetyl bromide forms solid solvates with organic tertiary bases and cadmium bromide. Pyridine, when mixed with ice-cold acetyl bromide, yields a very deliquescent red solid. Methylpyridines, except α-picoline and isoquinoline, also yields monosolvates, which are hygroscopic in nature. Cadmium bromide forms an unstable disolvate, which loses acetyl bromide slowly, and an intermediate solvate, $2CdBr_2.3AcBr$, has been analysed, which later on loses more of acetyl bromide under vacuum to yield a slightly more stable solvate, $2CdBr_2.AcBr$. The solvates isolated and the analytical results obtained are recorded in Table II.

TABLE IA

Quantitative solubilities in acetyl bromide at 30° ± 1°.

Compound.	Solubility (g./100 g. solvent).	Colour of solution.	Heat effect.	Compound.	Solubility (g./100 g. solvent).	Colour of solution.	Heat effect.
$SbBr_3$	120.3 g.	Black	..	$AsBr_3$	Miscible	Orange	..
$SnBr_4$	Miscible	..	..	α-Picoline	,,	Red	Exothermic
$TiBr_4$	,,	Red	Exothermic	Quinoline	,,	,,	,,
PBr_3	,,	..	..	Dimethylaniline	,,	Light yellow	,,
$HgBr_2$	0.772 g.	Dark red	..	$AlBr_3$	,,	Dark red	,,

TABLE IB

Qualitative solubilities.

Compound.	Solubility.	Colour.	Heat effect.
Bi_2O_3	Appreciable	Red	Exothermic
SeO_2	Highly soluble	Dark red	,,
CdO	Insoluble	Light yellow	,,
$CdCO_3$	,,	,,	,,
Li_2CO_3	,,	..	..
$AgNO_3$	,,	Reddish yellow	Exothermic
KNO_2	,,	Yellow	Slightly exothermic
Na_2CO_3	,,	Red	Exothermic.
$Na(CH_3COO)$	,,	Light yellow	,,
$UO_2(CH_3COO)_2$	Soluble	Black	,,
Pyridine.	Sparingly soluble	Red	,,
β-Picoline	,, ,,	,,	,,
γ-Picoline	,, ,,	Yellow	,,
Isoquinoline	,, ,,	,,	,,

Note : Miscible means freely soluble. Sparingly soluble and appreciably soluble signify the solubility of about 5% and 15% respectively.

TABLE II

Solvate formation.

Compound.	Solvate.	Colour.	Found.	Ratio.	Calc.	Ratio.
Pyridine	$C_5H_5N.CH_3COBr$	Red	*Base : 22.25 Br : 23.75	0.983	Base : 39.10 Br : 39.60	0.987
β-Picoline	$C_6H_7N.CH_3COBr$	,,	Base : 33.12 Br : 26.37	1.25	Base: 23.05 Br : 37.03	1.16
γ-Picoline	$C_6H_7N.CH_3COBr$	Yellow	Base : 29.16 Br : 23.43	1.22	Base: 43.05 Br : 37.03	1.16
Isoquinoline	$C_9H_7N.CH_3COBr$	,,	Base : 40.03 Br : 25.95	1.54	Base: 51.19 Br : 31.76	1.61
NN-Dimethyl-formamide	$C_3H_7CON.CH_3COBr$	..	..	..	(*loc. cit.*)	..
Cadmiun bromide	(*i*) $2CdBr_2.3CH_3COBr$	Dirty white	Cd : 24.23 Br : 59.67	..	Cd : 24.30 Br : 61.40	..
	(*ii*) $2CdBr_2.CH_3COBr$	,,	Cd : 33.70 Br : 58.36	..	Cd : 33.63 Br : 59.89	..

* The difference in the analytical results actually found and those calculated is due to the inert solvent, which has been used as a wash liquid and has been allowed to remain with the compound. The ratio of base/bromine in these cases is close enough to confirm the composition of the compounds.

The constitution of these solvates and of the solutions containing the Lewis acids and bases in acetyl bromide may be profitably discussed by taking into consideration the electrical properties of the solutions. The specific conductance of the Lewis acids, bases, and quaternary ammonium bromides has been determined in acetyl bromide at $30° \pm 0.1°$. The results are presented in Table III.

TABLE III

Specific conductance of the solutions of the Lewis acids and bases in acetyl bromide.

Specific conductance of acetyl bromide $= 2 \times 10^{-6}$ mhos.

Substance.	Conc. (mol./litre).	Conduc. (mhos).	Substance.	Conc. (mol./litre).	Conduc. (mhos).
Pyridine	0.01665	6.630×10^{-5}	Isoquinoline	0.00770	4.2900×10^{-5}
α-Picoline	0.01379	1.682×10^{-4}	$SnBr_4$	0.00228	8.0325×10^{-6}
β-Picoline	0.01108	0.531×10^{-4}	$SbBr_3$	0.01973	1.9460×10^{-5}
γ-Picoline	0.00428	2.3625×10^{-5}	Et_4NBr	0.01440	6.4200×10^{-4}

The specific conductance of the solutions of quaternary ammonium bromides in acetyl bromide indicates their strong ionisation in acetyl bromide; the result is almost comparable to that of potassium bromide in aqueous solutions. This increase in conductance of acetyl bromide in presence of these bromides is very likely due to the feeble ionisation of acetyl bromide to produce Br^- and Ac^+ ions. The addition of bromides results in an increase in the concentration of bromide ions, which conduct current. The mode of ionisation is exemplified as:

$$(C_2H_5)_4NBr \rightleftharpoons (C_2H_5)_4\overset{+}{N} + \overset{-}{Br}$$

Stannic bromide, which has been used as a Lewis acid in arsenic tribromide (Jander and Guenther, *Z. anorg. allgem. Chem.*, 1958, **297**, 81; 1959, **298**, 241), does not form any solid solvate with acetyl bromide and same is true of antimony tribromide. Of course, their addition to acetyl bromide enhances the specific conductance of the latter. The increase in conductance is presumably due to the formation of solvates in solution and their subsequent ionisation to provide acetylium ions as:

$$SnBr_4 + 2CH_3COBr \rightleftharpoons (SnBr_4.2CH_3COBr) \rightleftharpoons 2CH_3\overset{+}{C}O + SnBr_6^{2-}$$

$$SbBr_3 + CH_3COBr \rightleftharpoons (SbBr_3.CH_3COBr) \rightleftharpoons CH_3\overset{+}{C}O + SbBr_4^-$$

$$SbBr_3 + 3CH_3COBr \rightleftharpoons (SbBr_3.3CH_3COBr) \rightleftharpoons CH_3\overset{+}{C}O + SbBr_6.2CH_3CO^{2-}$$

$$\rightleftharpoons 2CH_3\overset{+}{C}O + SbBr_6.CH_3CO^{2-} \rightleftharpoons 3CH_3\overset{+}{C}O + SbBr_6^{3-}$$

The increase in conductance of acetyl bromide in presence of α-picoline, quinoline, and dimethylaniline, which do not form solid solvates under ordinary experimental conditions, is indeed interesting. These substances having tertiary nitrogen are presumed to form, in solution, solvates, which ionise furnishing cations containing quadrivalent nitrogen. Thus increase in conductance is due to the formation of strongly polar compounds, which furnish ions to conduct current. Bromide ions, which are considerably mobile, are more effective in carrying current.

$$\alpha\text{-}C_6H_7N + CH_3COBr \rightleftharpoons (C_6H_7N.CH_3COBr) \rightleftharpoons C_6H_7\overset{+}{N}.CH_3CO + \overset{-}{Br}$$

Similarly, the formation of solvates in solution and their subsequent ionisation are responsible for the increase in conductance of acetyl bromide when quinoline and dimethylaniline are added to the solution.

$$C_6H_5NMe_2 + CH_3COBr \rightleftharpoons (C_6H_5NMe_2.CH_3COBr) \rightleftharpoons C_6H_5\overset{+}{N}Me_2CH_3CO + \overset{-}{Br}$$

$$C_9H_7N + CH_3COBr \rightleftharpoons (C_9H_7N.CH_3COBr) \rightleftharpoons C_9H_7\overset{+}{N}CH_3CO + \overset{-}{Br}$$

The solvates of pyridine, isoquinoline, β-picoline, and γ-picoline, which are only slightly soluble in acetyl bromide, also enhance the conductance of acetyl bromide thus:

$$C_5H_5N + CH_3COBr \rightleftharpoons C_5H_5N.CH_3COBr \rightleftharpoons C_5H_5\overset{+}{N}.CH_3CO + \overset{-}{Br}$$

$$C_9H_7N + CH_3COBr \rightleftharpoons C_9H_7N.CH_3COBr \rightleftharpoons C_9H_7\overset{+}{N}.CH_3CO + \overset{-}{Br}$$

$$C_6H_7N + CH_3COBr \rightleftharpoons C_6H_7N.CH_3COBr \rightleftharpoons C_6H_7\overset{+}{N}.CH_3CO + \overset{-}{Br}$$

Behaviour of organic tertiary bases in acetyl chloride and benzoyl chloride has already been explained on similar lines (Paul *et al.*, *J. Chem. Soc.*, 1959, 315 ; this *Journal*, 1960, **37**, 195).

EXPERIMENTAL

Crude acetyl bromide was fractionated in an all-glass apparatus using a long fractionating oclumn. The fraction distilling at 73-75°/735 mm was collected, treated with purified dimethylaniline (1% by weight), and again fractionated using a long vacuum jacketed fractionating column filled with glass beads. The fraction coming at 74°/735 mm was collected. The distillate was further treated with freshly cut small pieces of sodium metal and distilled at a take-off ratio 1:10. Tertiary organic bases were purified as described previously (Paul *et al.*, *loc. cit.*, 1959).

To determine solubility of the various compounds in acetyl bromide, the latter was added with the help of a jet to a well-dried ampoule containing sufficient quantity of the compound ; but if the reaction was exothermic, the solid was added in small amounts to the thoroughly cooled acetyl bromide contained in the ampoule. The ampoule was immediately sealed and shaken in a thermostat controlled by a toluene regulator at 30° ± 0.1° for 24 hours. The ampoule was broken and the slurry formed was filtered quickly through a sintered glass funnel in absence of moisture. Solubility of the substance in 100 g. of acetyl bromide was determined by estimating the cation from the known weight of the solution.

The solvates of acetyl bromide with organic bases are mostly unstable. In such cases the thoroughly cooled base was slowly added to ice-cooled acetyl bromide contained in a standard joint test tube with the help of a dropper. After keeping the mixture in an ice bath for 2 hours, the solid was separated by filtration in a dry atmosphere and washed with dry benzene or dry petroleum ether. The compounds could not be kept under vacuum as these decomposed. The compounds were analysed as such. Bromine was estimated as silver bromide while bases were estimated by the Jackson-Smith method (*J. Amer. Chem. Soc.*, 1940, **62**, 544).

Cadmium bromide (5 g.) was treated with acetyl bromide (20 c.c.) in a sealed ampoule. The reaction mixture was shaken in a thermostat at 30° ± 0.1° for about 24 hours. The solid was separated by filtration and washed with dry benzene. Traces of the solvent were removed by keeping the solid under vacuum for 5 minutes. The solid was analysed when cadmium was estimated as cadmium molybdate and bromine as silver bromide. (Found : Cd, 24.23 ; Br, 59.67. $2CdBr_2.3CH_3COBr$ requires Cd, 24.3 ; Br, 61.4%).

The solvate was kept under vacuum for 2 hours and then again analysed. The results of analysis lead to the formula, $2CdBr_2.CH_3COBr$. (Found : Cd, 33.7 ; Br, 58.36. $2CdBr_2.CH_3COBr$ requires Cd, 33.63 ; Br, 59.89%).

Conductivity Outfit.—Precision measuring bridge type WBR. No. 108 with logarithmic amplifier type TAV, IKC, No. 034, manufactured by Wissenschaftlich Technische Werkstatten Wielheim/Oby., Germany, was used for determining conductance of the solutions. A solution of concentration about 0.01 moles/litre of different substances in acetyl bromide was directly prepared in the conductivity cell of a cell constant 0.315. All measurements were made at 30° ± 0.1° by placing the conductivity cell in a thermostat regulated to that temperature.

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Received November 26, 1960.

[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

Studies in Acetyl Bromide as a Polar Solvent. Part II. Solvolytic Reactions in Acetyl Bromide

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Solvolysis of a number of oxides, nitrates, nitrites, carbonates, and acetates has been studied quantitatively in acetyl bromide. A mechanism for solvolysis of these compounds, based on ionisation of acetyl bromide into acetylium and bromide ions, has been proposed.

In continuation of studies on acetyl bromide, solvolytic reactions providing useful information as to the polar nature of a solvent have been investigated. Solvolysis of oxides, nitrates, carbonates, acetates, etc. in acetyl bromide has been described. Selenium dioxide, which interacts vigorously with acetyl chloride under ordinary conditions to yield selenium tetrachloride along with a dark-coloured liquid (Singh, Paul and Sandhu, *J. Chem. Soc.*, 1959, 319), reacts with ice-cooled acetyl bromide to furnish a light yellow product in low yield. Analysis of this product, which decomposes slowly, confirms formation of selenium tetrabromide. The low yield of the product may be ascribed to side reactions involving selenium tetrabromide and acetic anhydride and to its high solubility in acetyl bromide (Morgan and Drew, *ibid.*, 1925, 531).

Stannic oxide reacts with acetyl bromide to form stannic bromide, which goes into solution. Formation of stannic bromide in solution has been confirmed by isolating its complex with tetraethylammonium bromide, the results of analysis of which are recorded in Table I.

Bismuth trioxide reacts with acetyl bromide to form a red solid, analysis of which leads to the composition $BiBr_3.2(CH_3CO)_2O$. Formation of similar addition compounds between acetic anhydride and metal chlorides has already been reported (Singh *et al.*, *loc.cit.*).

Cadmium oxide on refluxing with acetyl bromide for 8 hours yields a dirty white compound, which has been found to be a solvate of cadmium bromide with acetyl bromide. This solvate on heating to 160° yields almost pure cadmium bromide.

Calcium oxide and magnesium oxide are not completely solvolysed by acetyl bromide even on refluxing the mixture for a longer period as compared to the other oxides. Conversion of calcium oxide to bromide appears to be higher than that of magnesium oxide.

The mechanism of reactions between acetyl bromide and the oxides may be explained on the basis of an analogy with similar reactions in acetyl chloride (Singh *et al.*, *loc. cit.*). According to the views of McGookin and Page (*ibid.*, 1951, 2769) it is suggested that a primary reaction between an oxide and acetyl bromide results in the formation of an addition compound, which subsequently rearranges itself to produce acetic anhydride and metallic bromide.

$$SeO_2 + 4CH_3COBr \rightleftharpoons SeO_2.4CH_3COBr \rightleftharpoons SeBr_4.2(CH_3CO)_2O \rightleftharpoons SeBr_4 + 2(CH_3CO)_2O$$

In certain cases, e.g., bismuth oxide, calcium oxide, and magnesium oxide, an addition compound of acetic anhydride and metallic bromide is, however, obtained as the resultant product.

Solvolysis of silver nitrate has been reported in acetyl chloride (Singh *et al.*, *loc. cit.*). Acetyl bromide and finely powdered silver nitrate react vigorously at room temperature to yield silver bromide with copious evolution of brown fumes of the oxides of nitrogen. To ensure completion of this reaction, the mixture was refluxed for two hours. Acetyl bromide, as already proposed in Part I (this *issue*, p. 81), ionises as :

$$CH_3COBr \rightleftharpoons CH_3\overset{+}{C}O + Br^-$$

The mode of solvolytic reaction between acetyl bromide and silver nitrate can be expressed as :

$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^- \text{ (slightly soluble and feebly ionised)}$$

$$CH_3COBr \rightleftharpoons CH_3\overset{+}{C}O + Br^-$$

$$Ag^+ + \overset{-}{NO_3} + CH_3\overset{+}{C}O + Br^- \rightleftharpoons AgBr + CH_3CONO_3$$

Acetyl nitrate formed during this reaction decomposes to nitrogen dioxide or nitrosyl bromide and other products in presence of excess of acetyl bromide (Diels and Okada, *Ber.*, 1911, **44**, 3333).

$$4CH_3CONO_3 \rightleftharpoons 2(CH_3CO)_2O + 4NO_2 + O_2$$

$$2CH_3CONO_3 + 6CH_3COBr \rightleftharpoons 4(CH_3CO)_2O + 2NOBr + 2Br_2$$

Nitrates of barium and lead also yield the corresponding bromides ; the mode of the reaction may be explained on similar grounds.

Carbonates of lithium, copper, and cadmium are completely solvolysed with formation of the corresponding bromides. Lithium and copper carbonates yield anhydrous bromides, but cadmium carbonate, just like its oxide, produces a solvate of the formula $CdBr_2.\frac{1}{2}CH_3COBr$ while solvolysis of magnesium carbonate indicates conversion of the carbonate into the pure bromide with the oxide present as an impurity. The oxide undergoes solvolysis very slowly and its presence in the carbonate as an impurity may be the cause of incomplete solvolysis of magnesium carbonate. Absence of unsolvolysed carbonate has been proved by the non-existence of carbonate ions in the solvolysed product. The mode of solvolysis of carbonates, as exemplified by that of copper carbonate, is shown as :

$$CH_3COBr \rightleftharpoons CH_3\overset{+}{C}O + Br^-$$

$$CuCO_3 \rightleftharpoons Cu^{2+} + CO_3^{2-} \text{ (feebly soluble and ionised)}$$

$$Cu^{2+} + CO_3^{2-} + 2CH_3\overset{+}{C}O + 2\overset{-}{Br} \rightleftharpoons CuBr_2 + (CH_3CO)_2CO_3$$

Formation of insoluble copper bromide and unstable acetyl carbonate, the latter decomposing to acetic anhydride and carbon dioxide, favours the forward reaction :

$$(CH_3CO)_2CO_3 \rightleftharpoons (CH_3CO)_2O + CO_2$$

A study of the solvolysis of potassium nitrite and sodium sulphite also indicates complete conversion of these salts to bromides ; the mode of their reaction may be expressed as :

$$CH_3COBr \rightleftharpoons CH_3\overset{+}{C}O^+ + Br^-$$

$$KNO_2 \rightleftharpoons K^+ + \overset{-}{NO_2} \text{ (feebly soluble and ionised)}$$

$$CH_3\overset{+}{C}O + Br^- + K^+ + \overset{-}{NO_2} \rightleftharpoons KBr + CH_3CONO_2$$

Acetyl nitrite may decompose as :

$$CH_3CONO_2 + CH_3COBr \rightleftharpoons (CH_3CO)_2O + NOBr$$

$$\text{or } 2CH_3CONO_2 \rightleftharpoons (CH_3CO)_2O + NO_2 + NO$$

The interaction of sodium sulphite and acetyl bromide may be represented by the equations :

$$Na_2SO_3 \rightleftharpoons 2Na^+ + SO_3^{2-} \text{ (feebly soluble and ionised)}$$

$$CH_3COBr \rightleftharpoons \overset{+}{C}H_3CO + Br^-$$

$$2\overset{+}{C}H_3CO^+ + 2Na^+ + 2Br^- + SO_3^{2-} \rightleftharpoons 2NaBr + (CH_3CO)_2SO_3$$

Acetyl sulphite may decompose further to Ac_2O and SO_2 :

$$(CH_3CO)_2SO_3 \rightleftharpoons (CH_3CO)_2O + SO_2$$

Sodium and uranyl acetates form the corresponding bromides. Uranyl bromide is, however, associated with acetic anhydride, which is formed as a byproduct during solvolysis. A similar compound has been obtained during solvolysis of uranium trioxide in acetyl chloride (Chretien and Oeschoel, *Compt. rend.*, 1938, **206**, 254). Solvolysis of acetates can be expressed by taking into consideration the reaction between sodium acetate and acetyl bromide, expressed as :

$$CH_3COBr \rightleftharpoons \overset{+}{C}H_3CO + Br^-$$

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+ \text{ (feebly soluble and ionised)}$$

$$\overset{+}{C}H_3CO + Br^- + CH_3COO^- + Na^+ \rightleftharpoons NaBr + (CH_3CO)_2O$$

Formation of insoluble sodium bromide and undissociated acetic anhydride favours the forward reaction.

EXPERIMENTAL

Partial solvolysis of inorganic compounds was effected by mixing the substances with acetyl bromide in a sealed ampoule and keeping them at room temperature. In certain cases solvolysis went to completion even at room temperature, but in other cases for complete or maximum solvolysis, the following procedure was followed.

The well-dried solid (3-4 g.) was added to acetyl bromide (20-30 c.c.) in a 100 c.c. standard joint flask equipped with a water condenser and a guard tube to avoid moisture. The reaction mixture was refluxed on a water bath for a time depending on the nature of the compound ; acetyl bromide was replenished occasionally as required. The mixture was filtered in a dry atmosphere ; the solid was washed with a dry inert solvent and put in *vacuo* to evaporate excess of the solvent, and then analysed.

The reaction of selenium dioxide with acetyl bromide, which was violent, was performed at 0° ; contents were filtered after keeping the mixture for 2 hours in an ice bath. The solid was washed with dry petroleum ether (60-80°) and analysed as such because even under vacuum it showed decomposition. It is very much susceptible to moisture.

$SnBr_4$, formed on solvolysis of stannic oxide, remained in the solution of acetyl bromide. This was isolated as a complex by treating this solution with a tetraethylammonium bromide solution. The complex was analysed. The results prove that the complex is of the formula $(Et_4N)_2\ SnBr_6$, which can only be formed from $SnBr_4$. [Found : Br, 54.83 ; Sn, 13.97. $(Et_4N)_2\ SnBr_6$ requires Br, 55.89 ; Sn, 13.82%].

TABLE I

Compound.	Solvolysed product.	Colour.	Temp.	Time of reflux.	Found.	Calc.
SeO_2	$SeBr_4$	Red	0°	2 hrs.	Br: 65.13 Se: 17.77	80.20 19.79
SnO_2	$SnBr_4$	Red soln.	Reflux	4	..	..
Bi_2O_3	$BiBr_3.2Ac_2O$	Red	,,	4	Br: 35.12 Bi: 31.80	36.77 32.15
CdO	$CdBr_2$. ½AcBr	Dirty white	,,	8	Br: 58.16 Cd: 33.71	59.88 33.63
	$CdBr_2$	White			Br: 56.32 Cd: 38.40	58.74 41.25
CaO	$CaO.3\ CaBr_2.\ Ac_2O$	,,	,,	15	Br: 47.01 Ca: 15.92	49.89 16.63
MgO	$2MgO.MgBr_2.3Ac_2O$	,,	,,	10	Br: 27.34 Mg: 12.68	28.06 12.06
$AgNO_3$	AgBr	Yellow	,,	2	Br: 42.21 Ag: 56.94	42.55 57.44
$Ba(NO_3)_2$	$BaBr_2$	White	,,	8	Br: 52.70 Ba: 56.94	53.87 57.44
$Pb(NO_3)_2$	$PbBr_2$	Grey	,,	10	Br: 42.56 Pb: 56.57	43.59 56.40
$CuCO_3$	$CuBr_2$	Black	,,	6	Br: 69.21 Cu: 29.92	71.75 28.24
Li_2CO_3	LiBr	White	,,	25	Br: 91.40	91.95
$CdCO_3$	$CdBr_2$. ½AcBr	Dirty white	,,	8	Br: 59.20 Cd: 32.83	59.88 33.63
*$MgCO_3$	$xMgO.yMgBr_2.zAc_2O$	White	,,	8	Br: 28.98 Mg: 10.71	.. ..
KNO_3	KBr	,,	,,	6	Br: 58.00	57.22
Na_2CO_3	NaBr	,,	,,	8	Br: 78.80	77.66
CH_3COONa	NaBr	,,	,,	6	Br: 77.32	77.66
$UO_2(CH_3COO)_2$	$UO_2Br_2.2Ac_2O$	Black	,,	2	Br: 27.10 U: 35.99	25.27 37.44

* The product obtained after solvolysis gave no test for carbonate ions, showing thereby that magnesium carbonate had fully been solvolysed. But analysis showed that magnesium was in excess of that required for any formula of $MgBr_2$, $(CH_3CO)_2O$ and CH_3COBr, indicating the presence of some impurity of magnesium oxide in the product.

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Received November 26, 1960.

[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

Studies in Acetyl Bromide as a Polar Solvent. Part III. Formation of Acid/base Neutralisation Complexes in Acetyl Bromide

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Antimony tribromide, stannic bromide, and titanium tetrabromide, which act as solvo-acids in acetyl bromide, react with the ansolvo-bases (tetramethylammonium bromide, tetraethylammonium bromide, triethylbenzylammonium bromide, and dimethylethylphenylammonium bromide) and solvo-bases (quinoline, α-picoline, and dimethylaniline) to yield acid/base neutralisation complexes in acetyl bromide. The constitution of acidic and basic solutions in acetyl bromide has been discussed and the mode of formation of the acid/base neutralisation complexes, which have been isolated and analysed, indicated.

In the present investigations relating to the study of polar properties of acetyl bromide, complex compounds formed by the interaction of solvo-acids and solvo- and ansolvo-bases have been described. Acetyl bromide providing conducting solutions, when the Lewis acids, bases, and quaternary ammonium bromides are dissolved in it (Part I, this *issue*, p. 81), is indeed interesting so far its ionisation and the mode of ionisation of various substances in its solutions are concerned. The Lewis acids, antimony tribromide and stannic bromide, on dissolution increase conductance of acetyl bromide, which is due to the formation of solvo-acids, and their subsequent ionisation in solution. The mode of ionisation of solvo-acids, based on the conductance of their solutions in acetyl bromide and their behaviour in other solvents, may be expressed as :

$$SbBr_3 + CH_3COBr \rightleftharpoons (SbBr_3.CH_3COBr) \rightleftharpoons CH_3.\overset{+}{C}O + SbBr_4^-$$

or $$SbBr_3 + 3CH_3COBr \rightleftharpoons (SbBr_3.3CH_3COBr) \rightleftharpoons CH_3\overset{+}{C}O + (CH_3CO)_2SbBr_6^-$$

$$(CH_3CO)_2SbBr_6^- \rightleftharpoons CH_3\overset{+}{C}O + CH_3CO.SbBr_6^{2-}$$

$$CH_3CO.SbBr_6^{2-} \rightleftharpoons CH_3\overset{+}{C}O + SbBr_6^{3-}$$

In the present work only two upper stages of the ionisation have been realised and there is no indication of existence of the last stage.

$$SnBr_4 + 2CH_3COBr \rightleftharpoons (SnBr_4.2CH_3COBr) \rightleftharpoons CH_3\overset{+}{C}O + CH_3CO.SnBr_6^-$$

$$(CH_3CO)\,SnBr_6^- \rightleftharpoons CH_3\overset{+}{C}O + SnBr_6^{2-}$$

On analogous grounds behaviour of titanium tetrabromide may be anticipated to be as :

$$TiBr_4 + 2CH_3COBr \rightleftharpoons (TiBr_4.2CH_3COBr) \rightleftharpoons CH_3\overset{+}{C}O + CH_3COTiBr_6^-$$

$$CH_3CO.TiBr_6^- \rightleftharpoons CH_3\overset{+}{C}O + TiBr_6^{2-}$$

The quaternary ammonium bromides, such as tetraethylammonium bromide, triethylbenzylammonium bromide, etc., also considerably enhance conductance of acetyl bromide and are expected to act as ansolvo-bases (Part I, *loc. cit.*). The mode of their ionisation may be exemplified by that of tetraethylammonium bromide as :

$$(C_2H_5)_4NBr \rightleftharpoons (C_2H_5)_4\overset{+}{N} + Br^-$$

Organic tertiary bases, such as, α-picoline, quinoline, and dimethylaniline, also furnish solutions in acetyl bromide, which are more conducting than the pure solvent (Part I, *loc. cit.*).

This is interpreted to be due to ionisation of the solvo-bases formed. Actually, solvates of quite a few bases with acetyl bromide have already been isolated (Part I). Conductance of their solutions can only be due to their ionisation, which, keeping in view the strong electron-donor properties of nitrogen in the tertiary bases, can be represented as :

$$C_9H_7N + CH_3COBr \rightleftharpoons C_9H_7N.CH_3COBr \rightleftharpoons C_9H_7\overset{+}{N}.CH_3CO + \overset{-}{Br}$$

$$C_9H_7N + CH_3COBr \rightleftharpoons C_9H_7N.CH_3COBr \rightleftharpoons C_9H_7\overset{+}{N}.CH_3CO + \overset{-}{Br}$$

$$C_6H_5N.Me_2 + CH_3COBr \rightleftharpoons [C_6H_5N.Me_2CH_3COBr] \rightleftharpoons C_6H_5\overset{+}{N}.Me_2CH_3CO + \overset{-}{Br}$$

Antimony tribromide, dissolved in acetyl bromide, reacts with quaternary ammonium bromides to yield complexes of the type, R′ R″R‴ R⁗ N.$SbBr_4$.

Tetramethylammonium bromide is, however, an exception and formation of a compound of the formula $[(CH_3)_4N]_2(CH_3CO).SbBr_6$ takes place. This complex is obtained from triacetylium hexabromoantimonite as :

$$SbBr_3 + 3CH_3COBr \rightleftharpoons (SbBr_3.3CH_3COBr) \rightleftharpoons 2CH_3\overset{+}{C}O + CH_3CO.SbBr_6^{2-}$$

$$(CH_3)_4NBr \rightleftharpoons (CH_3)_4.\overset{+}{N} + \overset{-}{Br}$$

$$2(CH_3)_4\overset{+}{N} + 2\overset{-}{Br} + 2CH_3\overset{+}{C}O + CH_3CO.SbBr_6^{2-} \rightleftharpoons [(CH_3)_4N]_2.CH_3COSbBr_6 + 2CH_3COBr$$

A similar compound has been encountered in the study of conductometric titrations between tetraethylammonium bromide and antimony tribromide in acetyl bromide (Part IV, this *issue*, p. 93). The compounds of antimony tribromide with other quaternary ammonium bromides are shown in Table I.

α-Picoline, quinoline, and dimethylaniline react with antimony tribromide in acetyl bromide to yield compounds of the general type (B.CH_3CO)$SbBr_4$. Formation of the typical compound between antimony tribromide and α-picoline in acetyl bromide may be interpreted on the basis of ionic species as :

$$C_6H_7\overset{+}{N}.CH_3CO + \overset{-}{Br} + CH_3\overset{+}{C}O + SbBr_4^{-} \rightleftharpoons C_6H_7N.CH_3COSbBr_4 + CH_3COBr$$

The formation of feebly dissociated molecule of the solvent helps the reaction to completion.

Stannic bromide, which has been used as a dibasic solvo-acid in arsenic tribromide (Jander and Gunther, *Z. anorg. allgem. Chem.*, 1958, **297**, 81 ; 1959, **298**, 241), reacts with quaternary ammonium bromides in acetyl bromide to yield compounds of the general formula :

$$(R′\ R″\ R‴\ R⁗\ N)_2\ SnBr_6.$$

Its formation can be represented by a reaction between tetraethylammonium bromide and stannic bromide in acetyl bromide as :

$$2(C_2H_5)_4\overset{+}{N} + 2\overset{-}{Br} + 2CH_3\overset{+}{C}O + SbBr_6^{2-} \rightleftharpoons [(C_2H_5)_4N]_2SbBr_6 + 2CH_3COBr$$

Quinoline and diethylaniline, which form monoacid solvo-bases in acetyl bromide, react with stannic bromide to yield complexes of the general type $(B.CH_3CO)_2SnBr_6$. The mode of formation of these complexes may be represented as :

$$2B.CH_3CO + 2\overset{-}{Br} + 2CH_3\overset{+}{C}O + SbBr_6^{2-} \rightleftharpoons (B.CH_3CO)_2SnBr_6 + 2CH_3COBr$$

(B stands for a tertiary base.)

TABLE I

* Complexes.	Formula.	Colour.	M.P.	%Metal. Found.	%Metal. Calc.	%Bromine. Found.	%Bromine. Calc.	%Nitrogen. Found.	%Nitrogen. Calc.
Bis-tetramethyl Am acetylium HA	$[Me_4N]_2$. Ac. $SbBr_6$	Yellow	325-40°	15.99	15.37	60.03	60.54	1.82	1.76
Tetraethyl-Am TA	$(Et_4)N.\ SbBr_4$	,,	212-15°	20.40	21.30	55.73	55.98	2.67	2.45
Dimethylethylphenyl-Am TA	$(Me)_2N.\ Et.Ph.\ SbBr_4$	Light yellow	158-62°	19.07	20.05	53.04	53.07	2.46	2.36
Triethylbenzyl-Am TA	$Et_3N.\ C_7H_7.\ SbBr_4$	Yellow	125-28°	19.62	19.21	49.37	50.49	2.46	2.21
Dimethylphenylbenzyl-Am TA	$Me_2N.\ Ph.\ C_7H_7.\ SbBr_4$	,,	140-46°	18.92	18.63	48.99	48.94	2.48	2.14
Acetylquinolinium TA	$C_9H_7N.\ Ac.\ SbBr_4$	,,	185-88°	20.50	19.85	52.64	52.14	1.99	2.27
Acetyl-α-picolinium TA	$C_6H_7N.\ Ac.\ SbBr_4$	,,	92-112°	20.84	21.08	55.67	55.38	2.26	2.42
Acetyldimethylanilinium TA	$C_8H_{11}N.\ Ac.\ SbBr_4$	,,	104-10°	20.98	20.11	52.43	52.82	2.37	2.31
Bis-tetramethyl-Am HS	$[Me_4N]_2\ SnBr_6$	,,	320°	14.40	15.89	64.91	64.19	3.42	3.75
Bis-tetraethyl-Am HS	$[Et_4N]_2\ SnBr_6$	Light yellow	307°	13.97	13.82	55.49	55.89	3.06	3.26
Bis-dimethylethylphenyl-Am HS	$[Me_2N.\ Et.\ Ph]_2\ SnBr_6$	Yellow	207°	13.40	13.21	52.68	53.41	3.01	3.12
Bis-triethylbenzyl-Am HS	$[Et_3N.C_7H_7]_2\ SnBr_6$	,,	161-63°	12.16	12.08	48.57	48.84	3.03	2.85
Bis-dimethylphenylbenzyl-Am HS	$[Me_2N.C_6H_5.C_7H_7]_2\ SnBr_6$	Greenish yellow	172-85°	11.21	11.61	47.17	46.93	3.01	2.73
Bis-acetylquinolinium HS	$[C_9H_7N.Ac]_2\ SnBr_6$	Reddish pink	186-89°	12.96	12.59	50.09	50.90	2.63	2.97
Tris-acetyl-α-picolinium acetylinium bis-HS	$[C_6H_7N.Ac]_3\ (Ac)\ (SnBr_6)_2$	Yellow	152-55°	14.37	14.40	58.25	58.24	2.31	2.54
Tris-acetyldimethylanilinium acetylinium bis-HS hemi-acetyl bromide.	$(C_8H_{11}N.Ac)_3.Ac(SnBr_6)_2.$ $\frac{1}{2}$ AcBr	Dirty yellow	145-48°	13.13	13.23	55.36	55.74	2.19	2.34
Bis-acetyldiethylanilinium HS	$[PhN.Et_2]$ Ac. $2SnBr_6$	Light brown	..	12.14	12.05	48.99	48.85	2.73	2.85
Bis-tetramethyl-Am HT tetramethyl-Am bromide	$[Me_4N]_2TiBr_6.4Me_4NBr$	Brown	..	3.45	3.71	61.21	61.90	..	..
Bis-tetraethylammonium HT	$[Et_4N]_2\ TiBr_6$	Red	..	6.11	6.09	59.22	60.91	..	..
Bis-dimethylethylphenyl-Am HT	$[Me_2N.\ Et.\ Ph]_2\ TiBr_6$	,,	..	4.87 Br/Ti: 10.19	5.79 10.00	49.61	57.94	..	..
Bis-triethylbenzyl-Am HT	$[Et_3N.C_7H_7]_2\ TiBr_6$	Black	..	4.90	5.26	51.98	52.63	..	..
Bis-dimethylphenylbenzyl-Am HT	$[Me_2N.\ Ph.\ C_7H_7]_2\ TiBr_6$	Red	..	5.02	5.04	50.30	50.42	..	..

* Am denotes ammonium. HA & TA denote respectively hexa-and tetrabromo-antimonite. HS & HT denote respectively hexabromo-stannate and-titanate.

α-Picoline and dimethylaniline, which also form monoacid solvo-bases in acetyl bromide, react with stannic bromide to form complexes of the general formula $(B.CH_3CO)_3CH_3CO.(SnBr_6)_2$. These complexes appear to be equimolecular mixtures of the normal complexes $(B.CH_3CO)_2SnBr_6$ and the acid complex $(B.CH_3CO)\ (CH_3CO).SnBr_6$. The possible formation of the acid salt can be expressed as :

$$(B.CH_3CO)_2SnBr_6 + 2\overset{+}{C}H_3CO + SnBr_6^{2-} \rightleftharpoons 2B.CH_3CO.CH_3CO.SnBr_6$$

Titanium tetrabromide forms unstable and deliquescent complexes with the quaternary ammonium bromides, which can be expressed by the general formula $(R'\ R''\ R'''\ R''''\ N)_2TiBr_6$.

Formation of these complexes may be explained on the basis of ionic species, which exist in solutions. For instance :

$$2(C_2H_5)_3\overset{+}{N}.C_7H_7 + 2\overset{-}{B}r + 2CH_3\overset{+}{C}O + TiBr_6^{2-} \rightleftharpoons [(C_2H_5)_3N.C_7H_7]_2TiBr_6 + 2CH_3COBr$$

The complexes of organic tertiary bases with titanium tetrabromide are difficult to isolate as these are very much susceptible to moisture and decompose easily.

EXPERIMENTAL

Acetyl bromide, prepared from pure glacial acetic acid and phosphorus tribromide (Burton and Degering, *J. Amer. Chem. Soc.*, 1940, **62,** 227), was purified as described in preceding parts (*loc. cit.*).

Tetramethylammonium bromide, tetraethylammonium bromide, dimethylethylphenylammonium bromide, triethylbenzylammonium bromide, dimethylphenylbenzylammonium bromide, etc. were purified by crystallisation. These were analysed for bromide by Volhard's method in order to determine their percentage purity.

Quinoline, α-picoline, dimethylaniline, and diethylaniline were purified before use by refluxing them over KOH beads for about 2 hours in an all-glass apparatus, and finally distilling in an atmosphere of nitrogen. Titanium tetrabromide, stannic bromide, and antimony tribromide were purified by distillation in an all-glass apparatus.

General Procedure for Preparation of Acid/base Complexes

When the solutions of solvo-acids and solvo- or ansolvo-bases in acetyl bromide were mixed together, the acid/base neutralisation complexes were precipitated from the reaction mixture. Antimony complexes were precipitated by taking acids and bases in the ratio 1:1 in acetyl bromide. Stannic bromide reacted with bases in acetyl bromide in the ratio 1:2, resulting mostly in the formation of non-deliquescent, yellow complexes. Complexes of titanium tetrabromide with ansolvo-bases, such as tetraethylammonium bromide, etc., were isolated by mixing the components (acids and bases) in the ratio 1:2. All these complexes were filtered through a sintered glass funnel in a dry atmosphere and washed with dry benzene. These were kept under vacuum and analysed for bromine by Volhard's method. Titanium and tin were estimated as titanium dioxide and tin dioxide gravimetrically while antimony was determined iodimetrically. Nitrogen in the quaternary ammonium bromide complexes was analysed commercially while in the complexes of the Lewis acids with tertiary bases, nitrogen was determined by the Jackson and Smith method (*J. Amer. Chem. Soc.*, 1940, **62,** 544).

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Received November 26, 1960.

[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

Studies in Acetyl Bromide as a Polar Solvent. Part IV. Conductometric Titrations in Acetyl Bromide

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Existence of solvo-acids, solvo-bases, and ansolvo-bases in acetyl bromide, as already postulated, has been confirmed conductometrically in solutions. Stannic bromide and antimony tribromide have been used as solvo-acids. Solutions of α-picoline, quinoline, isoquinoline, and dimethylaniline have been used as solvo-bases and the quaternary ammonium halides, viz., tetraethylammonium bromide, triethylbenzylammonium bromide, dimethylethylphenylammonium bromide, and dimethylphenylbenzylammonium bromide, have been used as ansolvo-bases. The breaks in curves corresponding to different acid/base molar ratios have been noted, indicating the formation of acid or normal salts. Most of the complexes isolated in Part III have been confirmed and the formation of numerous others has been indicated. The formation of these complexes is explained on the basis of the existence of ionic species in the solutions of acetyl bromide.

In Part I of the series (this *issue*, p. 81) formation of the solvates of the Lewis acids and bases in acetyl bromide has been discussed and based on the conductance of their solutions, the ionisation of solvo-acids, solvo-, and ansolvo-bases has been indicated. The formation of acid/base neutralisation complexes, which have been isolated and analysed, has been presented in Part III of the series (this *issue*, p. 89). Recently conductometric titrations have gained considerable importance in the study of acid-base neutralisation reactions in polar solvents (Smith, *Chem. Rev.*, 1938, **23**, 165; Gutman, *Monatsh.*, 1954, **85**, 404; *Z. anorg.allgem.Chem.*, 1951, **266**, 331; Manhas *et al.*, *J. Chem. Soc.*, 1959, 325; Paul *et al.*, this *Journal*, 1960, **37**, 195). In the present work the acid-base neutralisation reactions have been studied conductometrically and the existence of complexes mentioned in Part III has been confirmed and that of quite a few new complexes has been indicated.

Addition of a solution of stannic bromide to that of tetraethylammonium bromide in acetyl bromide results in the formation of a yellow precipitate accompanied by a decrease in the conductance of the solution until it reaches a minimum at an acid/base molar ratio of 1:2 (Fig.1) at which the precipitation is complete. On further addition of the acid solution, the precipitate begins to dissolve and the conductance shows a sharp increase. A second break appears at acid/base molar ratio of 1:1. Here the dissolution of the precipitate is complete. Further addition of the acid brings about only a slight increase in the conductance, as is clear from the third portion of the curve (Fig. 1).

The changes in the value of conductance of the solution of tetraethylammonium bromide in acetyl bromide, with the addition of stannic bromide solution, may be interpreted in terms of the existence of ionic species in solution (Parts I and II, this *issue*, pp. 81, 85).

Tetraethylammonium bromide increases the conductance of acetyl bromide solution due to its ionisation as :

$$QBr \rightleftharpoons \overset{+}{Q} + Br^{-} \qquad .. \qquad .. \quad (1)$$

where Q stands for a quaternary ammonium radical. Since it increases the concentration of Br^{-} ions (anions specific of the solvent) it acts as an ansolvo-base. Addition of stannic bromide

to acetyl bromide also increases the conductance (Part I, *loc. cit.*), which may be explained on the basis of the formation of a solvo-acid in solution.

$$SnBr_4 + 2AcBr \rightleftharpoons SnBr_6^{2-} + 2Ac^+$$

Addition of the acidic solution to the basic solution results in the precipitation of the normal complex, bis-tetraethylammonium hexabromostannate. This results in the progressive removal of tetraethylammonium and bromide ions from solution with consequent decrease in conductance.

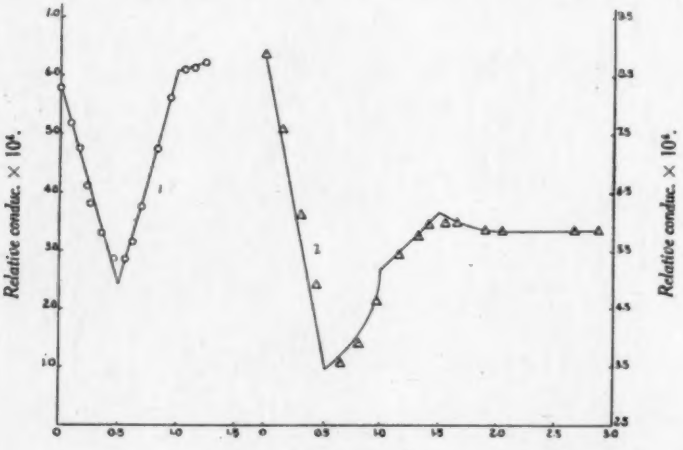
$$2\overset{+}{Q} + 2Br^- + 2Ac^+ + SnBr_6^{2-} \rightleftharpoons Q_2SnBr_6 + 2AcBr$$

The first break indicates the completion of this reaction. On further addition of the stannic bromide solution the precipitate of the normal complex begins to dissolve to form tetramethylammonium acetylhexabromostannate as follows :

$$Q_2SnBr_6 + Ac_2SnBr_6 \rightleftharpoons (2QAcSnBr_6) \rightleftharpoons 2Ac^+ + 2QSnBr_6^-$$

The acid salt, $QAcSnBr_6$, is more strongly ionised in solution than Q_2SnCl_6 or Ac_2SnCl_6. Its progressive formation results in an enormous increase in conductance of the solution. Once dissolution is complete, the conductance is only slightly affected by any further addition of the acid solution, which itself is comparatively feebly ionised.

FIG. 1



Molar ratio acid/base.

Curve 1: $SnBr_4/Et_4NBr$
Curve 2: $SbBr_3$/ ,,

The results of the titration of antimony tribromide with tetraethylammonium bromide are also represented in Fig. 1. The addition of antimony tribromide solution to that of tetraethylammonium bromide in acetyl bromide results in the formation of a precipitate and in an enormous decrease in conductance of the reaction mixture. This decrease continues to the point of minimum conductance where the acid/base molar ratio is 1:2 and the precipitation of the complex is complete. On further addition of the acid solution the precipitate begins to dissolve with a corresponding rise in conductance of the solution. At acid/base molar ratio of 1:1, the precipitate

is completely dissolved and there is a break in the curve. Further on, the rate of increase of conductance is much lower. There is a third break, which records maximum conductance at acid/base molar ratio of 3:2. After this the conductance again begins to decrease; possibly there is a fourth break at the acid/base molar ratio of 2:1. After this stage the conductance of the solution remains almost constant in spite of further additions of the acid solution.

Antimony tribromide is capable of acting as a monobasic acid and a tribasic acid where antimony is tetracovalent and hexacovalent. Formation of these four complexes can be explained on the basis of the hexacovalency of antimony :

$$SbBr_3 + 3CH_3COBr \rightleftharpoons SbBr_3.3CH_3COBr \text{ or}$$
$$\rightleftharpoons (CH_3CO)_3SbBr_6$$

The acid $(CH_3CO)_3SbBr_6$ can act as mono or dibasic acid depending on if one or two of the CH_3CO groups ionise :

$$(CH_3CO)_3SbBr_6 \rightleftharpoons (CH_3CO)_2SbBr_6^- + CH_3\overset{+}{C}O \rightleftharpoons CH_3CO.SbBr_6^{2-} + 2CH_3\overset{+}{C}O$$

Formation of the precipitate with the acid/base molar ratio of 1:2 may be represented as :

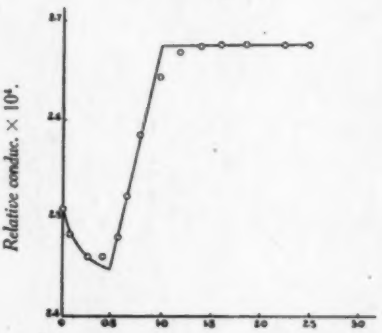
$$2(C_2H_5)_4\overset{+}{N} + 2Br^- + (CH_3CO)_3SbBr_6 \rightleftharpoons [(C_2H_5)_4N]_2CH_3COSbBr_6 + 2CH_3COBr$$

A complex of this type has been isolated with tetramethylammonium bromide in acetyl bromide (Part III, *loc. cit.*), which supports the formation of hexacovalent antimony. Further addition of the acid solution leads to the formation of 1:1 complex, $(C_2H_5)_4N.(CH_3CO)_2SbBr_6$, which has been isolated in its desolvated form $(C_2H_5)_4N.SbBr_4$ (Part III).

$$[Et_4N]_2.Ac.SbBr_6 + Ac_3SbBr_6 \rightleftharpoons 2Et_4N.\ Ac_2SbBr_6 \rightleftharpoons 2Et_4N.SbBr_4 + 4AcBr$$

In Fig. 2 the results of the conductometric titration of triethylbenzylammonium bromide with stannic bromide are presented. The curve shows the formation of the normal complex $[(C_2H_5)_3N\text{-}C_7H_7]_2.SnBr_6$ and the acid complex $(C_2H_5)_3N\text{-}C_7H_7.\ CH_3CO.\ SnBr_6$ corresponding to the breaks in the curve at acid/base molar ratio of 1:2 and 1:1 respectively. Formation of these complexes and their conductometric behaviour can be explained on the lines similar to those recorded for the titration of tetraethylammonium bromide against stannic bromide.

FIG. 2

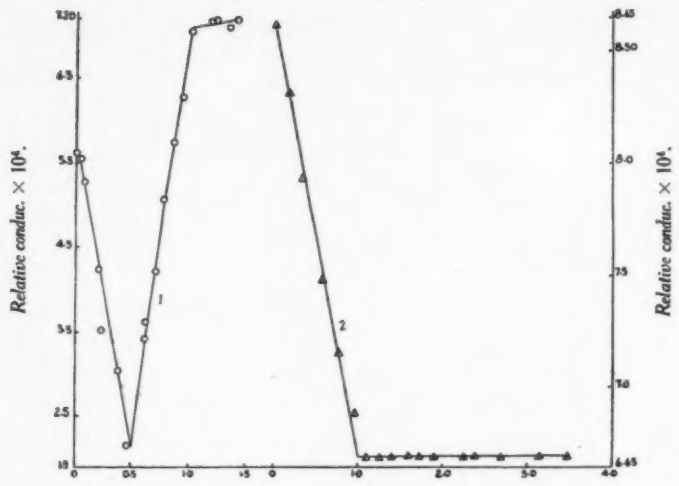


In Fig. 3 are shown the results of the titration of the solvo-acids, stannic bromide and antimony tribromide, against the ansolvo-base, dimethylethylphenylammonium bromide. The titration of stannic bromide against the quaternary ammonium bromide is exactly similar to its titration against tetraethylammonium bromide and shows formation of the normal complex with acid/base molar ratio of 1:2 and the acid salt with the acid/base molar ratio of 1:1.

Titration of antimony tribromide here is slightly different from the one with tetraethylammonium bromide. In the present case antimony tribromide acts as a monobasic acid, *i.e.*, the covalency of antimony is restricted to four.

$$CH_3COBr + SbBr_3 \rightleftharpoons CH_3\overset{+}{C}O + SbBr_4^-$$

FIG. 3



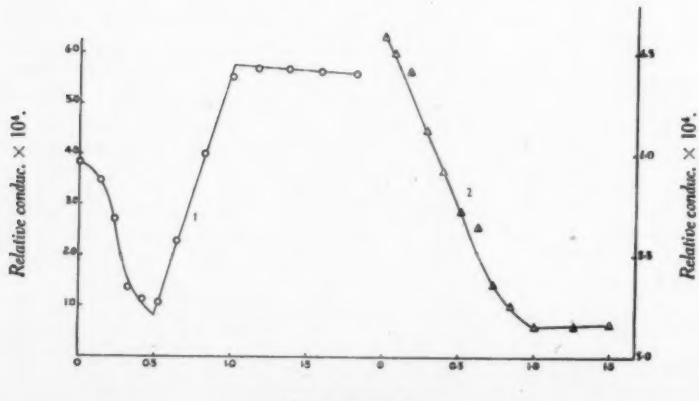
Molar ratio acid/base.

Curve 1: $SnBr_4/Me_2Et.Ph.NBr$
Curve 2: $SbBr_3$/ ,,

The conductance of the ansolvo-base decreases regularly with addition of the acid solution and a simultaneous separation of the normal complex, $(CH_3)_2N.C_2H_5.C_6H_5.SbBr_4$, till the first break at the acid/base molar ratio of 1:1 is reached. On further addition of the acid solution there is practically very little effect on the conductance of the solution since the acid solution is comparatively feebly ionised. The normal complex does not dissolve. These changes can be represented as :

$$\overset{+}{Q} + Br^- + Ac^+ + SbBr_4^- \rightleftharpoons QSbBr_4 + AcBr.$$

FIG. 4

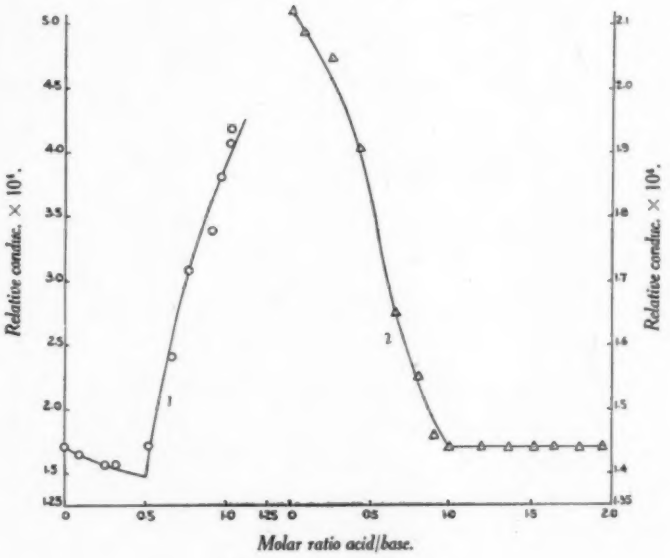


Molar ratio acid/base.

Curve 1: $SnBr_4/Me_2PhBzNBr$
Curve 2: $SbBr_3$/ ,,

In Fig. 4 are shown the conductometric titration curves of the titrations of the ansolvo-base, dimethylphenylbenzylammonium bromide, against the solvo-acids, stannic bromide and antimony tribromide. The curves obtained are very similar to those obtained in the case of dimethylethylphenylammonium bromide, as depicted in Fig 3, and can be explained exactly on similar lines.

FIG. 5



Curve 1: $SnBr_4$/α-picoline
Curve 2: $SbBr_3$/ „

α-Picoline, which has already been used as a solvo-base in acetyl chloride (Manhas *et al.*, *loc. cit.*), has been employed in the study of conductometric titrations with stannic bromide and antimony tribromide in acetyl bromide. The results obtained are plotted in Fig 5.

α-Picoline dissolves in acetyl bromide and gives a conducting solution (Part I, *loc. cit.*). This analogy with other tertiary bases can be explained on the basis of the formation of the solvate acetyl-α-picolinium bromide and its ionisation.

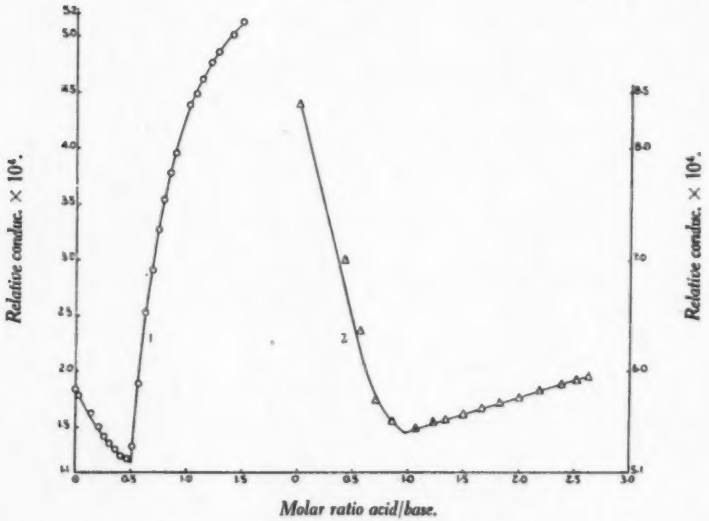
$$C_6H_7N + CH_3COBr \rightleftharpoons C_6H_7N.CH_3COBr \rightleftharpoons C_6H_7\overset{+}{N}.CH_3CO + Br^-$$

Addition of stannic bromide solution to that of α-picoline in acetyl bromide lowers the conductance of the latter with formation of a precipitate till a point of minimum conductance is reached at an acid/base molar ratio of 1:2 (Fig. 5).

$$2C_6H_7\overset{+}{N}.CH_3CO + 2Br^- + 2CH_3\overset{+}{C}O + SnBr_6^{2-} \rightleftharpoons (C_6H_7NCH_3CO)_2SnBr_6 + 2CH_3COBr$$

Any further addition of the stannic bromide solution increases the conductance, but, as expected, there is no second break; the precipitate formed does not dissolve in an excess of the acid solution. This leads to the conclusion that the acid salt formed is comparatively insoluble. The increase in conductance can be due to the formation and ionisation of the acid complex, $(C_9H_7N.CH_3CO)CH_3CO.SnBr_6$, which has some solubility. The existence of the normal complex, $(C_9H_7N.CH_3CO)_2SnBr_6$ has been proved by its isolation and chemical analysis (Part III).

FIG. 6



Curve 1: $SnBr_4$/quioline
Curve 2: $SbBr_3$/ „

The titration of α-picoline with antimony tribromide in acetyl bromide indicates only one break representing formation of the complex $(C_9H_7N.CH_3CO)SbBr_4$, existence of which has been proved in Part III (*loc. cit.*).

$$C_9H_7\overset{+}{N}.CH_3CO + Br^- + CH_3\overset{+}{C}O^+ + SbBr_4^- \rightleftharpoons (C_9H_7N.CH_3CO)SbBr_4 + CH_3COBr$$

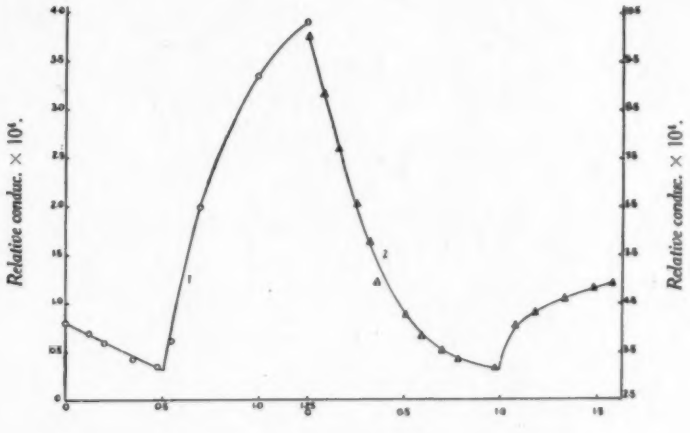
At acid-base molar ratio of 1:1 formation of the complex is complete and any further addition of the acid does not dissolve the precipitate. Further additions of the acid solution affect the conductance only slightly due to the feeble ionisation of the solvo-acid.

Results of the titrations of stannic bromide and antimony tribromide with quinoline are shown in Fig. 6. This shows the formation of the normal complexes $(C_9H_7N.CH_3CO)_2SnBr_6$ and $(C_9H_7N.CH_3CO)SbBr_4$. The formation of these complexes can be explained on similar lines as in the case of α-picoline. $(C_9H_7N.CH_3CO)SbBr_4$ has been isolated and analysed.

Results of the conductometric titrations of isoquinoline with stannic bromide and antimony tribromide in acetyl bromide are plotted in Fig. 7. Titrations with stannic bromide indicate

formation of only the normal complex, $(C_9H_7N.CH_3CO)_2SnBr_6$, *i.e.*, with acid/base molar ratio of 1:2. This complex also does not completely dissolve in an excess of the acid solution.

FIG. 7

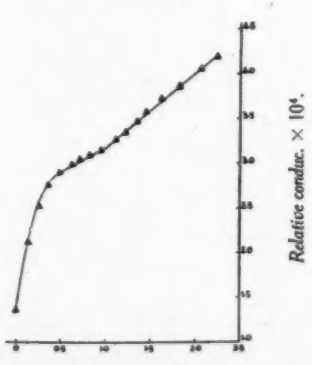


Curve 1: $SnBr_4$/isoquinoline
Curve 2: $SbBr_3$/ „

The titration of isoquinoline with antimony tribromide shows the formation of 1:1 compound (Fig. 7). The course of conductometric titration and the formation of complexes can be explained on similar lines as in the case of α-picoline.

Dimethylaniline has also been used as a base in acetyl bromide. Its titration with antimony tribromide is represented in Fig. 8. On addition of antimony tribromide solution to that of dimethylaniline in acetyl bromide, there is an increase in conductance till the acid/base molar ratio of 1:2 is reached, where there is a break in the curve. There is another break at the ratio of 1:1, beyond which the curve is again more steep. It has been noted for the first time in the present series that throughout the course of titration, an insoluble complex is not formed. This is a big difference as compared with the earlier titrations in all of which insoluble normal salt is formed resulting in a decrease of conductance. Here a change of species is represented by a change of the slope of the curve. The course of this curve can be explained by taking into account hexacovalency of trivalent antimony :

FIG. 8



$$2C_9H_{11}\overset{+}{N}.CH_3CO + 2Br^- + (CH_3CO)_2SbBr_6 \rightleftharpoons (C_9H_{11}N.CH_3CO)_2CH_3CO.SbBr_6 + 2CH_3COBr$$

$$(C_9H_{11}N.CH_3CO)_2CH_3CO.SbBr_6 + (CH_3CO)_2SbBr_6 \rightleftharpoons 2(C_9H_{11}N.CH_3CO)\,(CH_3CO)_2SbBr_6$$

EXPERIMENTAL

The solvent and the Lewis acids and bases were purified as already described (Part I, *loc. cit.*). For the present work acetyl bromide, purified as above, was again distilled through a special fractionating column and collected at a take-off ratio of 1:5.

A glass conductivity cell equipped with a microburette, replaceable platinum electrodes, and a calcium chloride guard tube was employed. The solutions were kept at a constant temperature by circulating water in the jacket of the cell from a thermostat maintained at $30° \pm 0.1°$. Stirring of the solution was done with the help of a magnetic stirrer. Resistance of the solutions was measured by using a precision measuring bridge of type WBR No. 108 with logarithmic indicator amplifier type TAV.IKC, No. 034 (Wissenschaftlich-Techniche Werkstatten, Weilheim/oby., Germany).

In Figs. 1-8 the molar ratio of acid/base has been plotted against the relative conductance, which is equal to $1/R$. The cell constant has not been taken into account due to the difficulty of placing the electrodes in exactly the same position in the cell. During the course of each titration the electrodes were, however, kept fixed.

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Received November 26, 1960.

[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

Studies on the Behaviour of Uni-bivalent Salts in Aqueous Solution. Part I. Potassium, Ammonium, Sodium, and Lithium Sulphates and Determination of Standard Electrode Potential of $Hg \mid Hg_2SO_4, SO_4^{2-}$

S. C. Sircar, P. K. Jena, and B. Prasad

The study of the cells of types (*a*) and (*b*) shows that sulphates of potassium, ammonium, sodium, and lithium are completely dissociated in aqueous solution up to 0.1 *M*. The study of the cells of types (*c*) and (*d*) confirms this view. In these cells 'M' stands for potassium, ammonium, sodium, or lithium and '*C*' for concentration in g. moles/litre. The standard electrode potential of the half cell, $Hg/Hg_2SO_4, SO_4^{2-}$, is found to be -0.6025 volt at 35°.

(*a*) Hg	Hg_2SO_4, M_2SO_4 (C_1)	salt bridge	M_2SO_4, Hg_2SO_4 (C_2)	Hg
(*b*) Hg	Hg_2SO_4, M_2SO_4 (C_1)	M_2SO_4, Hg_2SO_4 (C_2)	Hg	
(*c*) Hg	Hg_2Cl_2, MCl (2*C*)	saturated KCl bridge	M_2SO_4,Hg_2SO_4 (*C*)	Hg
(*d*) Hg	Hg_2Cl_2, MCl (2*C*)	M_2SO_4, Hg_2SO_4 (*C*)	Hg	

Righellato and Davies studied the dissociation of sulphates of K, Na, and Li (*Trans. Faraday Soc.*, 1930, **26**, 592) by the conductance method and computed the dissociation constant of

$$MSO_4^- \rightleftharpoons M^+ + SO_4^{2-}$$

to be 1.51×10^{-1}, 2.0×10^{-1}, and 2.29×10^{-1} respectively. They used some assumptions and approximations in their work. Their ideas have been checked with potentiometric measurements in the cells of the types :

(*a*) Hg	Hg_2SO_4,M_2SO_4 (C_1)	salt bridge	M_2SO_4,Hg_2SO_4 (C_2)	Hg
(*b*) Hg	Hg_2SO_4,M_2SO_4 (C_1)	M_2SO_4,Hg_2SO_4 (C_2)	Hg	
(*c*) Hg	Hg_2Cl_2,MCl (2*C*)	saturated KCl bridge	M_2SO_4,Hg_2SO_4 (*C*)	Hg
(*d*) Hg	Hg_2Cl_2,MCl (2*C*)	M_2SO_4,Hg_2SO_4 (*C*)	Hg	

(M stands for K, NH_4, Na, or Li)

EXPERIMENTAL

Mercurous sulphate from redistilled mercury was prepared by the electrolytic method of Hullet (*Phys. Rev.*, 1911, **32**, 257). It was washed with approximately $2N$-H_2SO_4 and stored under H_2SO_4 of the same concentration.

Mercurous chloride was prepared by adding a KCl solution to a solution of mercurous nitrate. The precipitate was washed with distilled water till free of nitrate, dried, and rubbed with pure mercury.

Stock solutions of K_2SO_4, $(NH_4)_2SO_4$, Na_2SO_4, KCl, NH_4Cl, and NaCl were prepared from B.D.H. AnalaR samples by directly weighing the salts. The strength of the sulphate solution was verified gravimetrically as barium sulphate. A stock solution of lithium sulphate was prepared from E.P. lithium sulphate and its strength was determined by estimating the sulphate gravimetrically as above. A stock solution of lithium chloride was prepared by adding a weighed amount of dry lithium carbonate (E.P.,E.Merck) to an exactly equivalent amount of dilute HCl (G.R.,E. Merck). Other solutions used in the experiments were prepared by diluting the stock solutions. Double distilled water was used in all experiments.

Cell vessels and salt bridges used and the method of checking of the half cells were the same as reported previously (this *Journal*, 1951, **28**, 683). For studying the E.M.F. of the cells of type (*a*), the two tested half elements, having different concentrations of M_2SO_4, were joined through a salt bridge consisting of saturated KCl or KBr. The E.M.F. values of the cells are recorded in Table I.

In cells of type (*b*) the two half elements having different concentrations of M_2SO_4 were joined through a U tube (*ibid.*, 1954, **31**, 490). The E.M.F. values are shown in Table II. The results on the cells of type (*c*) are shown in Table III and that of type (*d*) in Table IV.

In these studies, the E.M.F. readings were taken in duplicate at $35° \pm 0.1°$ and in every case the duplicates agreed within 0.2 mv.

TABLE I

Cell : type (*a*).

Conc. of sulphates.		E.M.F. with		Calc. E.M.F.	Diff. of columns (4) & (5).	E.M.F. with		Calc. E.M.F.	Diff. of columns (8) & (9).
C_1.	C_2.	KBr bridge.	KCl bridge.			KBr bridge.	KCl bridge.		
		Potassium sulphate.				Lithium sulphate.			
0.10*M*	0.02*M*	10.1mv	10.2mv	10.3mv	0.1mv	10.0mv	10.1mv	10.3mv	0.2mv
0.10	0.04	5.5	5.7	4.9	0.8	5.2	5.3	4.9	0.4
0.10	0.06	3.1	3.2	2.6	0.6	2.7	2.9	2.6	0.3
0.10	0.08	..	1.4	1.3	0.1	1.3	1.5	1.3	0.2
0.08	0.02	8.6	8.9	9.0	0.1	8.4	8.8	9.0	0.2
0.08	0.04	4.1	4.2	3.6	0.6	3.6	3.9	3.6	0.3
0.08	0.06	..	1.6	1.3	0.3	1.6	1.9	1.3	0.6
0.06	0.02	7.4	7.5	7.7	0.2	7.9	8.0	7.7	0.3
0.06	0.04	2.3	2.5	2.3	0.2	2.2	2.4	2.3	0.1
0.04	0.02	..	5.5	5.4	0.1	5.1	5.1	5.4	0.3
					Av. 0.31				Av. 0.29

TABLE I (contd.)

			Ammonium sulphate.			Sodium sulphate.			
0.10 *M*	0.02 *M*	..	10.3 mv	10.2 mv	0.1 mv	10.2 mv	10.2 mv	10.2 mv	0.0 mv
0.10	0.04	..	5.4	4.9	0.5	5.2	5.5	4.9	0.6
0.10	0.06	3.0 mv	3.1	2.6	0.5	..	3.0	2.6	0.4
0.10	0.08	1.3	1.3	1.3	0.0	..	1.5	1.3	0.2
0.08	0.02	8.8	8.9	8.8	0.1	8.2	8.6	8.8	0.2
0.08	0.04	4.1	4.1	3.6	0.5	3.8	4.0	3.6	0.4
0.08	0.06	..	1.5	1.3	0.2	..	1.6	1.3	0.3
0.06	0.02	7.4	7.5	7.7	0.2	..	7.2	7.7	0.5
0.06	0.04	..	2.5	2.3	0.2	..	2.5	2.3	0.2
0.04	0.02	5.3	5.3	5.4	0.1	4.7	4.8	5.4	0.6
					Av. 0.24				Av. 0.34

TABLE II

Cell : type (*b*).

Molar conc.		E.M.F. (in mv)			E.M.F. (in mv)			E.M.F.(in mv)			E.M.F.(in mv)		
C_1.	C_2.	Obs.	Calc.	Diff	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.
		Potassium sulphate.			Ammonium sulphate.			Sodium sulphate.			Lithium sulphate.		
0.04	0.02	10.5	10.5	0.0	9.9	10.6	0.7	..	..	..	7.5	7.6	0.1
0.06	0.04	5.7	6.0	0.3	5.5	5.9	0.4	4.5	4.9	0.4	4.0	4.2	0.2
0.08	0.06	4.2	4.2	0.0	3.9	4.1	0.2	3.2	3.4	0.2	3.0	2.9	0.1
0.10	0.08	3.1	2.8	0.3	2.9	2.8	0.1	2.6	2.3	0.3	2.3	2.0	0.3

TABLE III

Cell : type (*c*).

Molar conc.					Molar conc.				
SO_4^{2-}.	Cl^-	Obs. E''.	Calc. $-E_{Cl^-}$.	$-E_{SO_4^{2-}}$.	SO_4^{2-}.	Cl^-.	Obs. E''.	Calc $-E_{Cl^-}$.	$-E_{SO_4^{2-}}$.
		K_2SO_4 and KCl.					$(NH_4)_2SO_4$ and NH_4Cl.		
0.02	0.04	0.3099 volt	0.3565	0.6664 volt	0.02	0.04	0.3113 volt	0.3565	0.6678 volt
0.04	0.08	0.3223	0.3393	0.6616	0.04	0.08	0.3224	0.3393	0.6617
0.05	0.10	0.3261	0.3339	0.6600	0.06	0.12	0.3297	0.3294	0.6591
0.07	0.14	0.3322	0.3258	0.6580	0.07	0.14	0.3320	0.3288	0.6578
0.08	0.16	0.3339	0.3226	0.6565	0.08	0.16	0.3344	0.3225	0.6570
0.10	0.20	0.3386	0.3173	0.6559	0.10	0.20	0.3383	0.3173	0.6556
		Na_2SO_4 and NaCl.					Li_2SO_4 and LiCl.		
0.02	0.04	0.3104	0.3565	0.6669	0.02	0.04	0.3100	0.3565	0.6665
0.04	0.08	0.3220	0.3393	0.6613	0.04	0.08	0.3221	0.3393	0.6614
0.06	0.12	0.3295	0.3294	0.6589	0.05	0.10	0.3253	0.3339	0.6592
0.08	0.16	0.3344	0.3226	0.6570	0.07	0.14	0.3311	0.3258	0.6569
0.10	0.20	0.3380	0.3173	0.6553	0.10	0.20	0.3372	0.3173	0.6545

TABLE IV

Cell : types (*c*) and (*d*).

Molar conc. SO_4^{2-}.	Molar conc. Cl^-.	E'' of (type *c*).	E''' of (type *d*).	$E''-E'''$.	Molar conc. SO_4^{2-}.	Molar conc. Cl^-.	E'' of (type *c*).	E''' of (type *d*).	$E''-E'''$.
Potassium sulphate and potassium chloride.					Ammonium sulphate and ammonium chloride.				
0.02	0.04	0.3099 volt	0.3034 volt	0.0065 volt	0.02	0.04	0.3113 volt	0.3049 volt	0.0064 volt
0.04	0.08	0.3223	0.3154	0.0069	0.04	0 08	0.3224	0.3263	0.0061
0.05	0.10	0.3261	0.3200	0.0061	0.06	0.12	0.3297	0.3231	0.0066
0.07	0.14	0.3322	0.3257	0.0065	0.08	0.16	0.3344	0.3279	0.0065
0.08	0.16	0.3339	0.3274	0.0065	0.10	0.20	0.3383	0.3319	0.0063
0.10	0.20	0.3386	0.3316	0.0070	..	..	..	..	..
		Mean E_J = -0.0066 volt.					Mean E_J = -0.0064.		

TABLE V

Value of $E^\circ_{SO_4^{2-}}$ calc. from that of $E_{SO_4^{2-}}$ recorded in Table III.

Sulphate.	$-E_{SO_4^{2-}}$.	$-\frac{RT}{2F}\log_e a_{SO_4^{2-}}$.	$-E^\circ_{SO_4^{2-}}$.	Sulphate.	$-E_{SO_4^{2-}}$.	$-\frac{RT}{2F}\log_e a_{SO_4^{2-}}$.	$-E^\circ_{SO_4^{2-}}$.
Potassium sulphate.				Sodium sulphate.			
0.02*M*	0.6664 volt	0.0638	0.6026 volt	0.02*M*	0.6669	0.0638	0.6031
0.04	0.6616	0.0585	0.6031	0.04	0.6613	0.0585	0.6028
0.05	0.6600	0.0570	0.6030	0.06	0.6589	0.0560	0.6029
0.07	0.6580	0.0553	0.6027	0.08	0.6570	0.0545	0.6025
0.08	0.6565	0.0545	0.6020	0.10	0.6553	0.0534	0.6019
0.10	0.6559	0.0533	0.6026	..	..	..	..
		Mean $E^\circ_{SO_4^{2-}}$ = -0.6027 volt.				Mean value of E_0 = -0.6026.	
Ammonium sulphate.				Lithium sulphate.			
0.02*M*	0.6678	0.0638	0.6040*	0.02	0.6665	0.0638	0.6027
0.04	0.6617	0.0585	0.6032	0.04	0.6614	0.0585	0.6029
0.06	0.6591	0.0560	0.6031	0.05	0.6592	0.0570	0.6022
0.07	0.6578	0.0553	0.6025	0.07	0.6569	0.0553	0.6016
0.08	0.6570	0.0545	0.6025	0.10	0.6545	0.0533	0.6012†
0.10	0.6556	0.0534	0.6022	..	..	..	..

*Mean value of E_0 excluding the one asterisked = -0.6027.

†Neglected while taking the mean. Mean $E^\circ_{SO_4^{2-}}$ = -0.6024 volt.

N.B. Mean for all the four salts is -0.6026 volt.

DISCUSSION

Assuming that the liquid junction potential is eliminated by the salt bridge used, the E.M.F. values of the cells of type (*a*) for a particular salt can be represented by the equation :

$$E = \frac{RT}{2F}\log\frac{C_1 f_1^{2-}}{C_2 f_2^{2-}} \qquad .. \quad (1)$$

where C_1 and C_2 and f_1^{2-} and f_2^{2-} are respectively the concentrations and activity coefficients of the sulphate ion for various ionic strengths calculated from the mean activity coefficients

(Landolt-Börnstein, "Physikalisch-Chemische Tabellen", Roth and Scheel) of the sulphate and chloride concerned by the procedure followed earlier (*ibid*,. 1951, **28,** 683). Having known the activity coefficients, f_1^{2-} and f_2^{2-}, E, is calculated from equation (1), by assuming M_2SO_4 in solution to be dissociated completely to 0.10 M. The calculated values of E, recorded under columns 5 and 9 of Table I, agree fairly well with the observed E.M.F. shown under columns 3 & 7 (sat'd. KBr bridges) and 4(sat'd KCl bridge). Elimination of the liquid junction potential by saturated KCl or KBr bridge in the cells of type (*a*) has always been found nearly the same.

The E.M.F. of the cells of type (*b*) can be represented by

$$E' = \frac{3}{2} \cdot \frac{RT}{F} \cdot t^+ . \log \frac{C_1(f^{\pm})_1}{C_2(f^{\pm})_2} \qquad .. \qquad .. \quad (2)$$

where t^+ is the transport number of metal ion and C_1, C_2, $(f^{\pm})_1$ and $(f^{\pm})_2$ are respectively the concentrations and mean activity coefficients of M_2SO_4 at two different concentrations. The ionic conductances of K^+, NH_4^+, Na^+, Li^+, and $\frac{1}{2}$ SO_4^{2-} have been calculated to be 87.9, 88.5, 61.1, 49.7, and 95.0 at 35° from the data recorded by Glasstone (Electro-Chemistry of Solutions", 1945, p. 72). Transport numbers of these cations in their sulphates are found respectively to be 0.481, 0.482, 0.393, and 0.335 from the above data. With the transport numbers and the value of mean activity, the values of E' in these sulphates have been calculated from equation (2). The calculated values of E' are found to agree well with the observed data (Table II).

The study of the cells of types (*a*) and (*b*) conclusively demonstrates complete dissociation of the four sulphates in solution up to 0.10 M. To check this further and to determine the standard electrode potential, ($E^\circ_{SO_4^{2-}}$) of Hg | Hg_2SO_4, SO_4^{2-}, measurements of the E.M.F. values of the cells of types (*c*) and (*d*) were undertaken.

Assuming that the liquid junction potential is eliminated by saturated KCl bridge, the E.M.F (E'') of the cells of type (*c*) is represented by

$$E'' = E_{Cl^-} - E_{SO_4^{2-}} \qquad .. \qquad .. \quad (3)$$

where E_{Cl^-} is the E.M.F. of the Hg | Hg_2Cl_2, MCl half element and $E_{SO_4^{2-}}$ is that of the Hg | Hg_2SO_4, M_2SO_4 half element. The assumption about the elimination of liquid junction potential in cells of type (*c*) can be tested.

The E.M.F. (E''') of cells of type (*d*) are represented by

$$E''' = E_{Cl^-} - E_{SO_4^{2-}} + E_J \qquad .. \qquad .. \quad (4)$$

where E_J is the liquid junction potential developed between M_2SO_4 and MCl solutions. Equations (3) and (4) evidently show that if saturated KCl is able to eliminate the liquid junction potential, the difference of E''' and E'' should be equal to the value of E_J. E_J can be calculated from Henderson's equation, which reduces to the following form in the present conditions :

$$E_J = \frac{RT}{F} \cdot \frac{V_{Cl^-} - \frac{1}{2} V_{\frac{1}{2}SO_4^{2-}}}{V_{\frac{1}{2}SO_4^{2-}} - V_{Cl^-}} \log_e \frac{U_{M^+} + V_{Cl^-}}{U_{M^+} + V_{\frac{1}{2}SO_4^{2-}}} .$$

In the above equation V_{Cl^-} and $V_{\frac{1}{2}SO_4^{2-}}$ represent the ionic (equivalent) conductance of Cl^- and SO_4^{2-}, and U_{M^+} represents the conductance of K^+ or NH_4^+, depending on the type of cell used. Table IV shows that the average difference between E'' and E''' in the case of potassium salt is 6.6 mv and in ammonium salt, 6.4 mv. The calculated value of E_J for Henderson's equation comes out to be 6.1 mv in both cases. Hence, if there is any liquid junction potential, it is not likely to be beyond 0.5 mv. It may be assumed that l.j.p. is eliminated by saturated KCl in cells of type (*c*). Since the E.M.F. of these cells has been calculated on the basis of K_2SO_4 being completely dissociated in solution up to a concentration of 0.1 M, it might be safely concluded that K_2SO_4 is completely dissociated up to that concentration.

The value of $E^\circ_{Cl^-}$ (standard electrode potential of $Hg \mid Hg_2Cl_2, Cl^-$) is known at 18° and at 25°. By extrapolation the value is found to be -0.2659 at 35°. Now

$$E_{Cl^-} = E^\circ_{Cl^-} + \frac{RT}{F} \log_e C_{Cl^-} \cdot f_{Cl^-}.$$

The value of f_{Cl^-} for KCl, NH_4Cl, NaCl, and LiCl is taken to be the same as the mean activity coefficient of KCl at the same concentration. The value of E_{Cl^-} has thus been calculated (Table III). From this and the corresponding value of E'', recorded in these tables, $E_{SO_4^{2-}}$ has been calculated (Table III) and from the value of $E_{SO_4^{2-}}$, $E^\circ_{SO_4^{2-}}$ has also been calculated in Table V by using the equation :

$$E_{SO_4^{2-}} = E^\circ_{SO_4^{2-}} + \frac{RT}{2F} \log_e a_{SO_4^{2-}}.$$

The mean value of $E^\circ_{SO_4^{2-}}$, taking the four salts into consideration, is 0.6026 volt. $E^\circ_{SO_4^{2-}}$ can be also calculated in the four cases by using the Debye-Hückel limiting equation :

$$E_{SO_4^{2-}} = E^\circ_{SO_4^{2-}} + \frac{RT}{2F} \log_e C_{SO_4^{2-}} - \frac{RT}{2F} 4A \times 2.303 \sqrt{\mu} + \frac{RT}{2F} \cdot B\mu$$

where $A = 0.516$ at 35° and by plotting

$$E_{SO_4^{2-}} - \frac{RT}{2F} \log_e C_{SO_4^{2-}} + \frac{2RT}{F} \times 2.303 A\sqrt{\mu}$$

against μ. The extrapolated values for K_2SO_4, $(NH_4)_2SO_4$, Na_2SO_4 and Li_2SO_4 are -0.6026, -0.6025, -0.6021, and -0.6023 volt respectively, the mean of which is -0.6024 volt. Mean of the two methods is -0.6025 volt. The agreement of the two methods is very satisfactory. Our use of activity coefficient and complete dissociation up to a concentration of 0.1*M* in case of the four sulphates seems to be justified.

Correction in the concentration of sulphate ion due to the solubility of mercurous sulphate in the various sulphates is negligible.

The value of $E^\circ_{SO_4^{2-}}$ (-0.6025 volt) obtained in this work is 4.4 mv, lower than that obtained by Harned and Hamer (*J. Amer. Chem. Soc.*, 1935, **57**, 27) (-0.6070 volt at 35°), who determined $E^\circ_{SO_4^{2-}}$ at 0°, 15°, 25°, 40°, and 60° and represented their results by an equation having two constants. Their experimental value at 40° is 0.59900 ; the value calculated by their equation is 0.60305 and the difference comes to 4.05 mv. Their results can be better represented by the three-constant equation :

$$E_t^\circ = 0.63495 - 6.093 \times 10^{-4} \times t - 1.5157 \times 10^{-5} t^2 + 1.9794 \times 10^{-7} \times t^3.$$

Even with this equation the calculated value of E°_{25} comes to 0.61334 against the experimental value of 0.61514 and the difference is 1.8 mv. With three-constant equation, the value of E°_{35} comes to 0.6034 and differs from our value by 0.9 mv. When the difference between the calculated and observed values in Harned and Hamer's work comes to 4.05 mv with the first equation and 1.8 mv with the second equation, then the difference of 4.5 between the calculated value from the first equation and our value and the difference of 0.9 mv between our value and the value calculated from Harned and Hamer's work from the second equation becomes understandable. Hence our value (-0.6025) may be taken to be correct.

The authors express their thanks to the Government of India for the award of research training scholarships to two of them (S. C. Sircar & P. K. Jena).

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Received July 26, 1958.

[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

Amino Derivatives of Selenium Monobromide. Part II*

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The amino derivatives of selenium monobromide have been prepared by the action of the latter on some aromatic secondary and tertiary amines and heterocyclic bases. Properties of the derivatives have been studied and their structures discussed.

The preparation and properties of the compounds formed by the action of selenium monobromide on some aromatic primary amines have been studied in a previous communication (this *Journal*, 1960, **37**, 645). The work has been extended to study the action of selenium monobromide on some aromatic secondary and tertiary amines and heterocyclic bases under similar conditions.

EXPERIMENTAL

Selenium monobromide was prepared by the method of Lenher and Kao (*J. Amer. Chem. Soc.*, 1925, **47**, 772); other chemicals used were of E. Merck or B.D.H. 'extra pure' quality.

General Method of Preparation.—Solutions of selenium monobromide and the respective amines were prepared in CS_2; the amine solution was gradually added to the former with constant shaking till complete precipitation. The product formed was filtered, washed thoroughly with CS_2, and dried at the room temperature in a vacuum desiccator. Analyses and properties of the compounds studied are recorded in Table I.

Selenium was estimated as metallic selenium in a strong hydrochloric acid solution by reducing it with SO_2. Bromine was estimated by Piria and Schiff's method and nitrogen by Dumas' method in a Gallenkamp's electric furnace.

Properties.—The compounds formed with the secondary and tertiary amines and heterocyclic bases are in many respects similar to those formed with primary amines. These are generally coloured, amorphous, fairly stable, and practically insoluble in organic solvents. The compounds formed with diethylaniline and methylaniline are, however, hygroscopic and change in colour when kept in contact with moist air. These are hydrolysed very slowly in cold water, almost completely when boiled, and decompose when treated with dilute acids or alkalies.

On heating alone, the products furnish a greyish white sublimate, which is soluble in water; these are acidic and respond to the tests for bromine, :NH in secondary amines, and N : in tertiary amines. When these are heated with sodalime, the corresponding amines separate and condense in the cooler part of the tube, analogous to the behaviour of the compounds with primary amines.

The effective atomic number of selenium in these compounds is 36, which is a stable inert gas configuration and probably due to this the compounds are fairly stable.

The structure of these compounds appear to be similar to those formed with primary amines, as shown in Part I.

The authors' sincere thanks are due to the authorities of the Banaras Hindu University for providing necessary facilities.

* Part I: This *Journal*, 1960, **37**, 645.

TABLE I

Compounds of selenium monobromide with amines and heterocyclic bases.

Amine.	Product.	Colour.	M.P.	%Selenium.		%Bromine.		%Nitrogen.	
				Found.	Calc.	Found.	Calc.	Found.	Calc.
N-Methylaniline	$[Se_2(C_6H_5NHCH_3)_2]Br_2$	Green	140°	29.82	29.69	30.18	30.08	5.35	5.26
N-Ethylaniline	$[Se_2(C_6H_5NHC_2H_5)_2]Br_2$	Dirty white	188°	28.29	28.21	28.50	28.55	5.08	5.00
N-Benzylaniline	$[Se_2(C_6H_5NHCH_2C_6H_5)_2]Br_2$	Greyish black	136°	23.16	23.09	23.47	23.37	4.14	4.09
Diphenylamine	$[Se_2\{(C_6H_5)_2NH\}_2]Br_2$	Bluish black	129°	24.23	24.08	24.28	24.37	4.34	4.27
N-Dimethylaniline	$[Se_2\{C_6H_5N(CH_3)_2\}_2]Br_2$	Black	103°	28.13	28.21	28.49	28.55	5.02	5.00
N-Diethylaniline	$[Se_2\{C_6H_5N(C_2H_5)_2\}_2]Br_2$	Dark brown	157°	25.59	25.64	25.81	25.95	4.51	4.55
N-Dibenzylaniline	$[Se_2\{(C_6H_5CH_2)_2N.C_6H_5\}_2]Br_2$	Bluish black	123°	19.38	19.35	19.62	19.59	3.56	3.43
p-Amino-*N*-diethylanilin: .	$[Se_2\{(C_2H_5)_2N.C_6H_4NH_2\}_2]Br_2$	Black	209°	24.32	24.45	24.67	24.75	4.35	4.33
Quinoline	$[Se_2(C_9H_7N)_2]Br_2$	Brownish black	107°	27.48	27.42	27.71	27.76	4.95	4.86
Piperidine	$[Se_2(C_5H_{11}N)_2]Br_2$	Brick red	121°	32.49	32.37	32.70	32.77	5.80	5.74
Pyridine	$[Se_2(C_5H_5N)_2]Br_2$	Reddish black	135°	33.26	33.15	33.68	33.59	5.83	5.88
Piperazine	$[Se_2(C_4H_{10}N_2)]Br_2$	Brown	161°	32.35	32.24	32.69	32.63	5.69	5.71
α-Picoline	$[Se_2(C_6H_7N)_2]Br_2$	Pinkish gray	98°	31.39	31.35	31.65	32.73	5.67	5.55

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Received October 31, 1960.

[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

Iodometric Estimation of Formates by Oxidation with Iodine

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A new procedure is described for the volumetric determination of formate ion, based on its oxidation by iodine solution. The hydriodic acid liberated during oxidation is estimated by a standard potassium iodate solution. The procedure is applicable to neutral formate solutions containing 30 to 90 mg. of formic acid with a precision of 1% or more. The interference caused by the salts of other organic acids and organic substances has also been studied.

Fuchs (*Z. anal. Chem.*, 1929, **78,** 125), Oldeman (*Pharm. Weekblad.*, 1931, **68,** 379), and Bose (this *Journal*, 1958, **35,** 320) estimated neutral formates by oxidation with mercuric chloride solution and made subsequent determination of the acid produced during oxidation. The acidimetric estimation is interfered by carbon dioxide liberated during oxidation. Verma and Bose (this *Journal*, 1960, **37,** 47) volumetrically estimated the calomel produced by Andrew's method. The latter procedure is free from any interference caused by carbon dioxide. In the present method a formate solution is heated with an excess of iodine solution for a considerable time when it is oxidised by iodine according to the equation :

$$HCOONa + I_2 = HI + NaI + CO_2.$$

According to Dhar (*J. Chem. Soc.*, 1917, **111,** 726) the reaction occurs even at ordinary temperature with a measurable velocity. The hydrogen ions formed as a product of the change greatly retard the reaction. To obviate this Dhar used an excess of sodium acetate whereby the reaction became regular for kinetic study.

The reaction was found bimolecular, depending on the concentrations of formate ion and iodine. Iodide ion was also found to retard this oxidation reaction. In the present procedure potassium iodate solution was added to remove hydrogen ions, thus avoiding the use of a buffer, and iodine solution was prepared by adding minimum amount of KI to keep the iodide concentration low. The reaction was carried out at an elevated temperature (60-100°) and the hydriodic acid produced was estimated by adding an excess of a standard iodate solution. The reaction takes place in accordance with the equation :

$$KIO_3 + 6HI = KI + 3H_2O + 3I_2.$$

Later the residual potassium iodate was estimated by treating with an excess of H_2SO_4 and titrating the liberated iodine with a standard sodium thiosulphate solution. The amount of potassium iodate consumed affords the hydriodic acid liberated during the reaction and thus the amount of formate present is indirectly evaluated. ($6HCOOH \equiv 6HI \equiv KIO_3 \equiv 3I_2 \equiv 6Na_2S_2O_3$).

1 c.c. of $M/80$-KIO_3 solution=3.45 mg. of formic acid.

1 c.c. of $N/10$ sodium thiosulphate solution = 4.6 mg. of formic acid.

EXPERIMENTAL

Sodium thiosulphate, iodine, and starch were of A.R. quality ; potassium iodate was of Merck's variety and sodium formate was of B.D.H. A standard solution (0.025 *M*) of potassium iodate was prepared by dissolving 5.351 g. of the salt, dried at 120° for 1 hour, in 1 litre of water. Standard solutions of sodium formate were prepared by dissolving different amounts of the salt after drying at 100° for 1 hour.

The other solutions prepared were 0.5*N* and 0.025*N* sodium thiosulphate, 0.4*N* iodine (containing 75 g. of potassium iodide per litre), and 1% aqueous starch. *M*/80-KIO_3 solution was prepared by diluting the *M*/40 solution.

Procedure.—To a neutral solution (10 to 20 c.c.) of formate containing about 30 to 90 mg. of formic acid, taken in a 250 c.c. conical flask, a standard solution of potassium iodate was added in a known excess. 0.4*N* Iodine solution (10 c.c.) was also introduced in the flask and the total volume was made to 40 c.c. The flask was kept immersed in an electrical water bath, containing water at 25°, and weighted by encircling its lower portion by a band of lead. About two third of the flask was under water. The rate of heating the bath was so adjusted that 10 to 12 minutes were required to start boiling. The flask was kept in boiling water for 30 minutes after the start of boiling so that the total period of heating was 40 minutes. The flask was then taken out and cooled under tap. A 0.5*N* sodium thiosulphate solution was gradually added from a burette till the solution in the flask was faint yellow. At this stage 1 c.c. of starch solution was added and the iodine was precisely neutralised with *N*/40 thiosulphate solution. The contents of the flask were acidified by adding about 2c.c. of 1*N*-H_2SO_4; the liberated iodine was titrated with a standard thiosulphate solution. A blank was also carried out in exactly similar manner except for the addition of the formate solution. The difference between two hypo readings gave iodate consumed in terms of hypo equivalent. The results for the evaluation of different formate solutions are recorded in Table I. All the estimations were carried out in duplicate.

TABLE I

Formic acid	Present (mg.)	92.0	82.8	69.0	55.2	46.0	32.2
	Found (mg.)	92.3	83.5	69.6	55.4	46.3	32.0
	%Error	0.4	1.0	0.9	0.4	0.7	-0.6

Effect of change in the time of heating, in the amount of water, and in the concentration of iodine solution was studied. The results are recorded in Tables II, III, and IV respectively.

TABLE II

Effect of change in the period of boiling.

(10 c.c. of *M*/10 formate solution+20 c.c. of *M*/80-KIO_3 solution+10c.c. of 0.4*N* iodine solution)

Time after start of boiling.	Total period of heating.	Formic acid. Present.	Found.	%Error.
10 mins.	22 mins.	46.0 mg.	46.4 mg.	+0.9
20	32	,,	46.4	+0.9
28 (recommended)	40	,,	46.1	+0.3
40	52	,,	46.1	+0.3
60	72	,,	46.0	±0.0
90	102	,,	46.1	+0.3

Total time of heating for 30 to 40 minutes was found suitable. It was found necessary to adjust the rate of heating in a way that the time required for boiling to start was about 10 to 12 minutes.

TABLE III

Effect of increase in the amount of water.

(10 c.c. of $M/10$ formate solution + different amounts of water + 20 c.c. of $M/80$-KIO_3 solution + 10 c.c. of 0.4N-I_2 solution). Total time of heating = 40 mins.

Water added.	Total volume.	Formic acid.		%Error.
		Present.	Found.	
0.0 c.c.	40.0 c.c. (recommended)	46.0	46.1	+0.3
10.0	50.0	„	46.3	+0.7
20.0	60.0	„	46.8	+1.8
30.0	70.0	„	47.6	+3.6
40.0	80.0	„	48.0	+4.8
50.0	90.0	„	48.5	+5.3

Increase in the amount of water resulted in higher values for formate. Best results were obtained when the total volume was about 40 c.c.

TABLE IV

Effect of change in the concentration of iodine.

(10 c.c. of $M/10$ formate solution + 10 c.c. of $M/40$-KIO_3 solution + different amounts of iodine solution). Total volume = 40 c.c. Total time of heating = 40 mins.

0.4N-I_2 soln. added.	Water added.	Formic acid.		%Error.
		Present.	Found.	
5.0 c.c.	15.0 c.c.	46.0 mg.	45.3 mg.	−1.5
7.5	12.5	„	46.2	+0.5
10.0 (recommended)	10.0	„	46.2	+0.5
12.5	7.5	„	46.4	+0.9
15.0	5.0	„	46.9	+2.0
20.0	0.0	„	48.3	+5.0

7.5 to 10 c.c. of 0.4N iodine solution proved suitable for 46 mg. of formic acid. For the estimation of formate solution containing 30 to 90 mg. of formic acid, 10 c.c. of 0.4N iodine solution was used.

Interference.—Table V shows the interference caused by salts of organic acids and other organic substances. Glucose, benzaldehyde, and sodium salicylate showed profound interference and all the iodate added was consumed while addition of borax resulted in low values for formate so that almost all the iodate remained unchanged. This is probably due to the buffering of hydrogen ions by this salt.

TABLE V

(10 c.c. of $M/10$ sodium formate + 20 c.c. of $M/80$-KIO_3 solution + substance + 10 c.c. of 0.4N iodine solution). Total time of heating = 40 mins. Sodium formate added = 68.0 mg.

Expt. No.	Substance added.	Sodium formate found.	%Error.
1.	EtOH (1 c.c.)	73.3 mg.	+ 8.0
2.	CCl_4 „	72.3	+ 6.5
3.	K-citrate (0.2 g.)	57.8	−15.5
4.	Ca-gluconate „	72.9	+ 7.5
5.	„ lactate „	73.6	+ 8.5
6.	„ butyrate „	60.0	−12.0
7.	Formaldehyde „	96.4	+42.6
8.	Acetaldehyde „	79.4	+17.0
9.	Salicylaldehyde „	87.7	+29.5
10.	Na-tartarate „	67.5	− 0.7
11.	„ acetate (in equimol. conc.)	66.8	− 1.7
12.	„ malonate (containing 0.2 g. of acid)	64.3	− 5.5
13.	„ benzoate „	72.8	+ 7.2
14.	„ adipate „	45.4	−34.0
15.	„ fumarate „	67.0	− 1.0
16.	„ maleate „	14.3	−80.5
17.	„ malate „	62.5	− 8.2
18.	„ phenylacetate „	67.5	− 0.7
19.	„ aminoacetate „	64.3	− 5.5
20.	„ propionate (equimol. proportion)	67.0	− 1.5

In the above procedure potassium iodate solution serves two purposes—estimation of hydriodic acid produced and removal of hydrogen ions. Addition of a buffer is not necessary. The disadvantage of the method lies in the interference caused by a large number of substances. Sodium acetate or propionate, if present in equimolar concentration, does not interfere much. In presence of large concentrations of these salts of homologues of formic acid, the method fails probably due to the buffering action of acetate and propionate ions, which prevent the hydriodic acid produced from reacting with potassium iodate. Hence this procedure is recommended for the estimation of neutral solutions of formates in absence of oxidisable impurities. The procedure being iodometric is simple and exhibits a sharp end point.

The thanks of the authors are due to Principal Umadas Mukerji for providing the facilities needed for this work.

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Received December 7, 1960.

[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

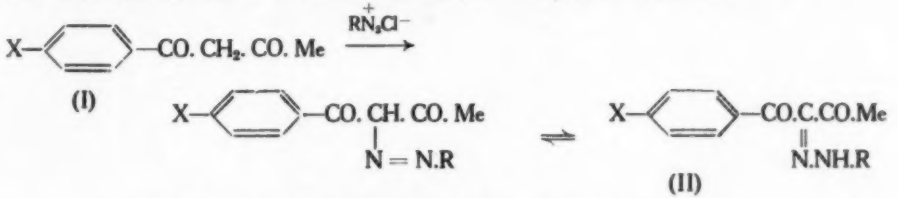
Reactive Methylene Compounds. Part V*. Condensations with Benzenediazonium Salts

H. G. Garg**

Behaviour of several benzenediazonium chlorides with different benzoylacetones has been studied. The characteristics of the derivatives formed are described.

The earlier communication on the coupling of aromatic diazonium salts with reactive methylene compounds (Garg and Joshi, this *Journal*, 1960, **37**, 626) was prompted by the desire to determine the structure of the stable form.

The present investigation includes the preparations of some so-called benzeneazo derivatives of benzoylacetones. These derivatives have been synthesised by reacting a few benzenediazonium chlorides with 4-substituted benzoylacetones, namely, 4-chloro-(I:X = Cl), 4-bromo-(I:X = Br), 4-methyl-(I:X = Me) and 4-methoxy-(I:X = OMe) benzoylacetones.



[X = Cl, Br, Me or OMe ; R = phenyl or substituted phenyl]

The rate of coupling of various benzoylacetones with a particular benzenediazonium chloride has been found different. The rate of reaction increases when chloro and bromo groups are present in the *para* position in the phenyl group; other group, such as, Me or OMe, decreases the rate of reaction.

All these compounds are highly coloured, crystalline solids, develop red colour with H_2SO_4 (conc.), and are precipitated as such on dilution. These are soluble in ethanol, acetic acid, benzene, etc.

EXPERIMENTAL†

4-Bromo-(Hanus *et al.*, *Coll. Czech. Chem. Comm.*, 1929, **1**, 392), 4-chloro-(Hauser *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 4023), 4-methyl-(Basu, this *Journal*, 1931, **8**, 119), and 4-methoxy-(Horeau and Jacques, *Bull. Soc. Chim.*, 1948, 53) benzoylacetones were prepared from the corresponding acetophenones by condensation with ethyl acetate with the aid of sodium in dry ether.

Benzeneazo-4-chlorobenzoylacetone.—Aniline (0.05*M*) was diazotised in the usual manner and the filtered diazonium chloride solution was run into a cooled, stirred mixture of crystalline sodium acetate (50 g.) and 4-chlorobenzoylacetone (0.05*M*) in water (25 c.c.) and ethanol (25 c.c.). Benzeneazo-4-chlorobenzoylacetone began to separate immediately. It was collected after 8 hours and recrystallised from acetic acid. Different derivatives are described in Table I.

Benzeneazo-4-bromobenzoylacetones (Table I), benzeneazo-4-methylbenzoylacetones (Table II), and benzeneazo-4-methoxybenzoylacetones (Table II) were similarly prepared.

Author's sincere thanks are due to Dr. S. S. Joshi, D. Sc., Director, School of Chemistry and Principal, Meerut College, Meerut, for his interest and to the Ministry of Scientific Research and Cultural Affairs, Government of India, for a research fellowship.

* Part IV : This *Journal*, 1960, **37**, 626.

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† Melting points are uncorrected.

TABLE I

No.	Substituted benzeneazo derivative formed.	4-Chlorobenzoylacetone. Yield.	M.P.	Colour.	Formula.	%Chlorine. Found.	Calc.	4-Bromobenzoylacetone. Yield.	M.P.	Colour.	Formula.	%Bromine. Found.	Calc.
1.	Benzeneazo	88%	144°	Light brown	$C_{16}H_{13}O_2N_2Cl$	11.72	11.81	89%	150°	Light red	$C_{16}H_{13}O_2N_2Br$	22.98	23.19
2.	4-Methoxy-	84	122°	Golden yellow	$C_{17}H_{15}O_3N_2Cl$	10.31	10.74	84	132°	Light orange	$C_{17}H_{15}O_3N_2Br$	21.03	21.33
3.	4-Bromo-	92	140°	Light ,,	$C_{16}H_{12}O_2N_2BrCl$	30.19*	30.43	92	138°	Yellow	$C_{16}H_{12}O_2N_2Br_2$	37.34	37.73
4.	4-Chloro-	91	147°	Dirty ,,	$C_{16}H_{12}O_2N_2Cl_2$	20.92	21.19	92	142°	Brownish yellow	$C_{16}H_{12}O_2N_2BrCl$	*30.13	30.43
5.	3-Chloro-	93	114°	Light ,,	$C_{16}H_{12}O_2N_2Cl_2$	20.83	21.19	91	121°	Yellow	$C_{16}H_{12}O_2N_2BrCl$	*30.21	30.43
6.	2-Chloro-	91	144°	Pale ,,	$C_{16}H_{12}O_2N_2Cl_2$	20.76	21.19	..	..	..	..	..	..
7.	4-Nitro-	95	181°	Dirty ,,	$C_{16}H_{12}O_4N_3Cl$	9.81	10.27	95	184°	Dirty yellow	$C_{16}H_{12}O_4N_3Br$	20.23	20.51
8.	3-Nitro-	91	140°	Dirty ,,	$C_{16}H_{12}O_4N_3Cl$	9.78	10.27	..	..	..	..	..	..
9.	4-Methyl-	84	124°	Canary ,,	$C_{17}H_{15}O_2N_2Cl$	10.91	11.28	84	125°	Golden yellow	$C_{17}H_{15}O_2N_2Br$	22.11	22.28
10.	3-Methyl-	..	..	..	..	..	..	83	134°	Yellow	$C_{17}H_{15}O_2N_2Br$	21.98	22.28
11.	2-Chloro-4-nitro-	91	192°	Pale yellow	$C_{16}H_{11}O_4N_3Cl_2$	18.58	18.68	91	178°	Dirty yellow	$C_{16}H_{11}O_4N_3BrCl$	*26.84	27.20
12.	2-Nitro-4-chloro-	90	190°	Light orange	$C_{16}H_{11}O_4N_3Cl_2$	18.48	18.68	90	198°	Canary yellow	$C_{16}H_{11}O_4N_3BrCl$	*26.91	27.20

* Br+Cl.

TABLE II

*No.	Yield.	M.P.	Colour.	4-Methylbenzoylacetone. Formula.	Found.	Calc.	Yield.	M.P.	Colour.	4-Methoxybenzoylacetone. Formula.	Found.	Calc.
1.	86%	148°	Pale yellow	$C_{17}H_{16}O_2N_2$	N : 9.82%	10.00%	85%	138°	Pale yellow	$C_{17}H_{16}O_3N_2$	N : 9.32%	9.45%
2.	84	132°	Light orange	$C_{18}H_{18}O_2N_2$	N : 8.92	9.03	83	126°	Golden ,,	$C_{18}H_{18}O_4N_2$	N : 8.33	8.58
3.	91	138°	Canary yellow	$C_{17}H_{15}O_2N_2Br$	Br : 22.01	22.28	..	..	..	..	..	..
4.	91	112°	Do.	$C_{17}H_{15}O_2N_2Cl$	Cl : 11.11	11.28	91	116°	Canary ,,	$C_{17}H_{15}O_3N_2Cl$	Cl : 10.38	10.74
5.	90	124°	Light ,,	$C_{17}H_{15}O_2N_2Cl$	Cl : 10.84	11.28	90	128°	Canary ,,	$C_{17}H_{15}O_3N_2Cl$	Cl : 10.41	10.74
6.	91	126°	Golden ,,	$C_{17}H_{15}O_2N_2Cl$	Cl : 10.91	11.28	90	137°	Yellow	$C_{17}H_{15}O_3N_2Cl$	Cl : 10.41	10.74
7.	95	116°	Light ,,	$C_{17}H_{16}O_4N_2$	N : 12.61	12.92	94	141°	Do.	$C_{17}H_{16}O_5N_2$	N : 12.12	12.31
8.	92	114°	Light ,,	$C_{17}H_{16}O_4N_2$	N : 12.72	12.92	93	165°	Do.	$C_{17}H_{16}O_5N_2$	N : 12.29	12.31
9.	..	..	..	..	..	..	..	..	..	..	..	..
10.	83	112°	Yellow	$C_{18}H_{18}O_2N_2$	N : 9.09	9.52	82	124°	Canary ,,	$C_{18}H_{18}O_3N_2$	N : 8.98	9.03
11.	91	198°	Canary ,,	$C_{17}H_{14}O_4N_2Cl$	Cl : 9.57	9.87	92	195°	Yellow	$C_{17}H_{14}O_5N_2Cl$	Cl : 9.12	9.45
12.	90	184°	Pale ,,	$C_{17}H_{14}O_4N_2Cl$	Cl : 9.48	9.87	91	192°	Yellow-orange	$C_{17}H_{14}O_5N_2Cl$	Cl : 9.28	9.45

* The number of benzeneazo derivatives corresponds to those in Table I.

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Received November 12, 1960.

[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

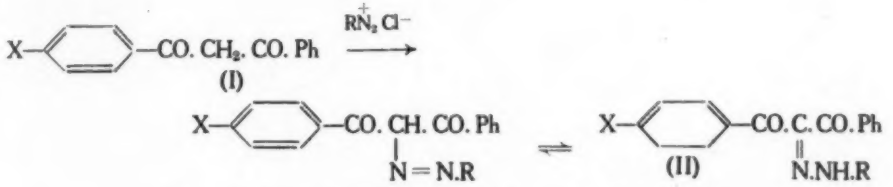
Received November 12, 1960.

Reactive Methylene Compounds. Part VI. Condensations with Benzenediazonium Salts

H. G. Garg*

Several 4-substituted dibenzoylmethanes have been coupled with benzenediazonium salts to furnish the corresponding benzeneazo-4-substituted dibenzoylmethanes.

In continuation of the previous work (Garg *et al.*, this *Journal*, 1960, **37**, 626) the coupling of benzenediazonium chlorides with 4-substituted dibenzoylmethanes, such as, 4-chloro-(I:X = Cl), 4-methyl-(I:X = Me), 4-bromo-(I:X = Br), 4-nitro- (I:X = NO_2) dibenzoylmethanes, has now been studied.



[X = Cl, Br, Me or NO_2 ; R = phenyl or substituted phenyl]

The so-called benzeneazo derivatives obtained are highly coloured, crystalline solids, and are soluble in ethanol, benzene, acetic acid, etc. These develop red colour with concentrated sulphuric acid and are precipitated as such on dilution.

EXPERIMENTAL**

The syntheses of 4-chloro-, 4-bromo-, 4-methyl- and 4-nitro- dibenzoylmethanes were easily effected by the action of sodium methoxide on dibromides of substituted benzylideneacetophenones (Bodforss, *Ber.*, 1918, **51,** 214 ; Barnes and Dodson, *J. Amer. Chem. Soc.*, 1943, **65,** 1585).

Benzeneazo-4-chlorodibenzoylmethane.—Aniline (0.05*M*) was diazotised in the usual manner ; the filtered diazonium chloride solution was run into a cooled, stirred mixture of crystalline sodium acetate (50 g.) and 4-chlorodibenzoylmethane (0.05*M*) in ethanol (100 c.c.). Benzeneazo-4-chlorodibenzoylmethane separated immediately and was collected after 10 hours. It was recrystallised from acetic acid. Different derivatives are described in Table I.

Benzeneazo-4-bromodibenzoylmethanes (Table I), benzeneazo-4-methyldibenzoylmethanes (Table II), and benzeneazo-4-nitrodibenzoylmethanes (Table II) were similarly prepared.

Author's sincere thanks are due to Dr. S. S. Joshi, Principal, Meerut College, Meerut, for his interest and to the Ministry of Scientific Research and Cultural Affairs, Government of India, for a research scholarship.

* Present address : Central Drug Research Institute, Lucknow.

** Melting points are uncorrected.

TABLE I

No.	Substituted benzeneazo derivative.	4 Chlorodibenzoylmethane. Yield.	M.P.	Colour.	Formula.	%Halogen. Found.	Calc.	4-Bromodibenzoylmethane. Yield.	M.P.	Colour.	Formula.	%Halogen. Found.	Calc.
1.	Beneneazo-	86%	130°	Yellow	$C_{21}H_{15}O_2N_2Cl$	9.61	9.79	89%	153°	Golden yellow	$C_{21}H_{15}O_2N_2B_1$	19.43	19.65
2.	4-Methoxy-	84	148°	Canary-yellow	$C_{22}H_{17}O_3N_2Cl$	9.12	9.04	86	189°	Orange	$C_{22}H_{17}O_3N_2Br$	18.14	18.30
3.	4-Bromo-	90	163°	Yellow	$C_{21}H_{14}O_2N_2BrCl$	25.98	26.16	92	205°	Golden yellow	$C_{21}H_{14}O_2N_2Br_2$	32.81	32.92
4.	4-Chloro-	89	186°	Canary-yellow	$C_{21}H_{14}O_2N_2Cl_2$	17.63	17.88	91	202°	Yellow	$C_{21}H_{14}O_2N_2BrCl$	26.01	26.16
5.	3-Chloro-	89	168°	Golden yellow	$C_{21}H_{14}O_2N_2Cl_2$	17.71	17.88	91	160°	Orange	$C_{21}H_{14}O_2N_2BrCl$	26.10	26.16
6.	2-Chloro-	..	..	..	..	..	..	90	154°	Dirty yellow	$C_{21}H_{14}O_2N_2BrCl$	26.10	26.16
7.	4-Nitro-	94	221°	Yellow	$C_{21}H_{14}O_4N_3Cl$	8.52	8.71	95	196°	Golden yellow	$C_{21}H_{14}O_4N_3Br$	17.51	17.69
8.	3-Nitro-	92	170°	Light yellow	$C_{21}H_{14}O_4N_3Cl$	8.62	8.71	94	159°	Pale yellow	$C_{21}H_{14}O_4N_3Br$	17.48	17.69
9.	4-Methyl-	84	168°	Yellow	$C_{22}H_{17}O_2N_2Cl$	9.28	9.42	86	186°	Yellow	$C_{22}H_{17}O_2N_2Br$	18.88	19.00
10	3-Methyl -	84	169°	Light yellow	$C_{22}H_{17}O_2N_2Cl$	9.19	9.42	86	151°	Orange	$C_{22}H_{17}O_2N_2Br$	18.79	19.00
11.	2-Chloro-4-nitro-	92	198°	Canary-yellow	$C_{21}H_{13}O_4N_3Cl_2$	15.91	16.06	91	212°	Pale yellow	$C_{21}H_{13}O_4N_3BrCl$	23.51	23.74
12.	2-Nitro-4-chloro-	91	182°	Yellow	$C_{21}H_{13}O_4N_3Cl_2$	15.82	16.06	91	180°	Yellow	$C_{21}H_{13}O_4N_3BrCl$	23.62	23.74

TABLE II

*No.	4-Methyldibenzoylmethane. Yield.	M.P.	Colour.	Formula.	Found.	Calc.	4-Nitrodibenzoylmethane. Yield.	M.P.	Colour.	Formula.	Found.	Calc.
1.	87%	123°	Yellow	$C_{22}H_{18}O_2N_2$	N: 7.92%	8.18%	..	..	..	..	..	..
2.	85	124°	Pale yellow	$C_{23}H_{20}O_2N_2$	N: 7.32	7.52	83%	175°	Yellow-orange	$C_{22}H_{17}O_5N_3$	N: 10.38%	10.42%
3.	90	153°	Golden yellow	$C_{22}H_{17}O_2N_2Br$	Br: 18.81	19.00	89	205°	Yellow	$C_{21}H_{14}O_4N_3Br$	Br: 17.48	17.69
4.	89	152°	Yellow	$C_{22}H_{17}O_2N_2Cl$	Cl: 9.13	9.42	88	214°	Do.	$C_{21}H_{14}O_4N_3Cl$	Cl: 8.48	8.71
5.	89	140°	Golden yellow	$C_{22}H_{17}O_2N_2Cl$	Cl: 9.11	9.42	87	182°	Pale yellow	$C_{21}H_{14}O_4N_3Cl$	Cl: 8.38	8.71
6.	..	..	..	..	..	..	86	193°	Yellow	$C_{21}H_{14}O_4N_3Cl$	Cl: 8.52	8.71
7.	94	168°	Yellow	$C_{22}H_{17}O_4N_3$	N: 10.62	10.85	..	..	..	..	..	..
8.	93	162°	Do.	$C_{22}H_{17}O_4N_3$	N: 10.71	10.85	..	..	..	..	..	..
9.	85	156°	Golden yellow	$C_{23}H_{20}O_2N_2$	N: 7.62	7.86	..	..	..	..	..	..
10.	..	..	..	..	..	..	..	..	..	..	..	..
11.	91	182°	Pale yellow	$C_{22}H_{16}O_4N_3Cl$	Cl: 8.12	8.42			Yellow			
12.	90	188°	Golden yellow	$C_{22}H_{16}O_4N_3Cl$	Cl: 8.21	8.42	88	> 250°	..	$C_{21}H_{13}O_6N_4Cl$	Cl: 7.62	7.84

* The number of benzeneazo derivatives corresponds to those listed in Table I.

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Received November 28, 1960.

[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

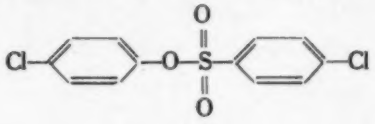
Organic Pesticides. Part V*. Synthesis of Certain Fluorodiaryl Sulphonates and Hydroxydiaryl Sulphones

K. C. Joshi and S. Giri

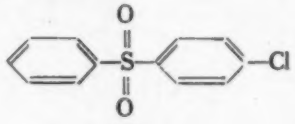
Several fluorodiaryl sulphonates and hydroxydiaryl sulphones, derived from *p*-fluorophenol and *p*-cresol, have been prepared as potential pest-control chemicals.

In view of the insecticidal and fungicidal properties of Ovotran (I) and Sulphenone (II) and consequent screening of the activity of a large number of their structural analogues (Metcalf, "Organic Insecticides", p. 197; Szabo and Oswald, *Hung. Tech. Abst.*, 1955, **7,** No. 1 ; *Chem. Abst.*, 1957, **51,** 14593 ; Keller *et al.*, *J. Econ. Entomol.*, 1957, **50,** 141 ; Frear, "Chemistry of Pesticides", p. 29 ; Dutch Pat. 81/1956 ; *Chem. Abst.*, 1959, **53,** 3588), we have now synthesised several fluoro analogues of Ovotran (I) and converted them to the corresponding hydroxydiaryl sulphones of type (III), expecting that a combination of toxic phenolic function with Ar-SO_2-Ar moiety in the latter might enhance their pesticidal activity.

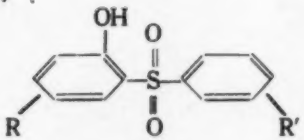
Although non-fluoro compounds of type (III) have been prepared by several workers (Simons *et al.*, *J. Amer. Chem. Soc.*, 1940, **62,** 485 ; Amin and Desai, *J. Sci. Ind. Res.*, 1954, **13B,** 181 ; Sen and Roy, this *Journal*, 1956, **33,** 687 ; Balliah *et al.*, *ibid.*, 1959, **36,** 391) very little work has been done on analogous fluorine compounds. Certain fluorobenzyl phenyl sulphones have, however, been patented by Boots Pure Drug Co. (B.P. 792,045/1958) as acaricides.



(I)



(II)



(III)

In this communication we report the preparation of eleven diaryl sulphonates (eight from *p*-flourophenol and three from *p*-cresol) by the method of Sen and Roy (*loc. cit.*) by the interaction of aryl sulphonyl chlorides and appropriate phenol in acetone-alkali solution. *p*-Fluorophenol has been obtained from *p*-anisidine by the Balz-Schiemann reaction. The aryl sulphonyl chlorides have been prepared by the chlorosulphonation of the appropriate hydrocarbon by following the method of Huntress and Carten (*J. Amer. Chem. Soc.*, 1940, **62,** 511). The sulphonates have been rearranged by the Fries reaction at 130-40° (Amin and Desai, *loc. cit.*) to yield the corresponding hydroxydiaryl sulphones.

EXPERIMENTAL

p-Fluoroanisole was prepared by the method of English *et al.* (*J. Amer. Chem. Soc.*, 1940, **62,** 350) from *p*-anisidine (60 g.) ; yield 29 g. (47.5%). Its b.p. corresponds to that previously recorded.

*Part IV : This *Journal*, 1960, **37,** 687.

TABLE I

No.	Hydrocarbon.	Aryl sulphonyl chlorides. Sulphonyl chloride.	M.P./B.P. Obs.	M.P./B.P. Lit.	Aryl sulphonamides. Sulphonamide.	M.P. Obs.	M.P. Lit.	Formula.	% Sulphur. Found.	% Sulphur. Calc.
1.	Chlorobenzene	4-Chlorobenzene-	51-52°	53.5°	4-Chlorobenzene-	142°	142-43°	$C_6H_6O_2NClS$	16.02	16.71
2.	Fluorobenzene	4-Fluorobenzene-	32-33°	30°	4-Fluorobenzene-	124°	124-25°	$C_6H_6O_2NFS$	17.46	18.28
3.	*p*-Dichlorobenzene	2, 5-Dichlorobenzene-	35-36°	38°	2, 5-Dichlorobenzene-	178-80°	180°	$C_6H_5O_2NCl_2S$	13.62	14.16
4.	*p*-Dibromobenzene	2, 5-Dibromobenzene-	70-71°	71°	2, 5-Dibromobenzene-	194°	194-95°	$C_6H_5O_2NBr_2S$	9.66	10.16
5.	*p*-Bromofluorobenzene	2-Bromo-5-fluorobenzene-	62-63°	..	2-Bromo-5-fluorobenzene-	137-38°	..	$C_6H_5O_2NBrFS$	11.98	12.59
6.	*p*-Fluorotoluene	2-Methyl-5-fluorobenzene-	155-58°/50 mm	145-50°/0 mm	2-Methyl-5-fluorobenzene-	139°	140-41°	$C_7H_6O_2NFS$	16.10	16.93
7.	α-Fluoronaphthalene	4-Fluoronaphthalene-	85-87°	86°	4-Fluoronaphthalene-	205°	206°	$C_{10}H_8O_2NFS$	13.72	14.22

p-Fluorophenol was obtained by demethylation of *p*-fluoroanisole (28 g.); yield 13 g. (52%), b.p. 185-87°. Finger *et al.* (*ibid.*, 1959, **81**, 94) report b.p. 185-86°.

Fluorobenzene was prepared by the Balz-Schiemann reaction (Vogel, "A Text Book of Practical Organic Chemistry", p. 609) from aniline (46.5 g.); yield 19 g. (36.6%), b.p. 82-83.5°. Heilbron and Bunbury ("Dictionary of Organic Compounds", p. 548) report b.p. 85.2°.

p-Bromofluorobenzene was prepared by the above method from *p*-bromoaniline (21.5 g.); yield 15 g. (68.7%), b.p. 150-52°. Heilbron and Bunbury (*ibid.*, p. 549) report b.p. 151.6-51.9°/755 mm.

α-Fluoronaphthalene was obtained by the above method from α-naphthylamine (25 g.); yield 13 g. (50.9%), b.p. 63-65°/5 mm. Heilbron and Bunbury (*ibid.*, p. 554) report b.p. 80°/11 mm.

Aryl sulphonyl chlorides were prepared by the method of Huntress and Carten (*loc. cit.*). The hydrocarbon (10 g.), dissolved in chloroform (50 c.c.), was chlorosulphonated at 0-5° with chlorosulphonic acid (50 g.). The contents after half an hour were poured over crushed ice. The chloroform layer separating was removed and the aryl sulphonyl chloride was isolated (solid or liquid). In some cases, chlorosulphonation was incomplete in cold and hence refluxing from 30 to 90 minutes was felt desirable. The aryl sulphonyl chlorides thus prepared were characterised as sulphonamides.

Aryl sulphonamides were prepared by the method of Huntress and Carten (*loc. cit.*). The aryl sulphonyl chloride (2 g.) was boiled for 30-40 minutes with strong ammonia (20 c.c.) and the mixture poured into cold water; the precipitated sulphonamide was isolated as usual and recrystallised from aqueous ethanol. The aryl sulphonyl chlorides and their corresponding sulphonamides are listed in Table I.

TABLE II

4-Fluorophenyl aryl sulphonates.

No.	Aryl.	M.P./B.P.	%Yield.	Formula.	% Sulphur. Found.	Calc.
1.	4'-Methylphenyl	56-57°	81.0	$C_{13}H_{11}O_3FS$	11.52	12.03
2.	4'-Chlorophenyl	101-02°	72.4	$C_{12}H_8O_3ClFS$	11.20	11.17
3.	4'-Fluorophenyl	74-75°	63.5	$C_{12}H_8O_3F_2S$	11.18	11.85
4.	2',5'-Dichlorophenyl	240-42°/40-50 mm	56.0	$C_{12}H_7O_3Cl_2FS$	9.28	9.97
5.	2',5'-Dibromophenyl	41-42°	52.0	$C_{12}H_7O_3Br_2FS$	7.17	7.80
6.	2'-Bromo-5'-fluorophenyl	180-81°/30-35	49.3	$C_{12}H_7O_3BrF_2S$	8.61	9.17
7.	2'-Methyl-5'-fluorophenyl	205°/2-3	52.7	$C_{13}H_{10}O_3F_2S$	10.92	11.27
8.	4'-Fluoronaphthyl	65°	67.0	$C_{16}H_{10}O_3F_2S$	9.53	10.00

Diaryl sulphonates were prepared by following the method of Sen and Roy (*loc. cit.*). To an ice-cold solution of acetone, containing aryl sulphonyl chloride (1.1*M*) and phenol (1 *M*), was added a 10% aqueous NaOH solution in excess with frequent shaking. The sulphonates slowly settled down as solid or liquid except in a few cases where keeping overnight was necessary. These were washed till free of alkali and either recrystallised from aqueous ethanol or distilled under reduced pressure. The sulphonates obtained are recorded in Tables II and III.

TABLE III

4-Methylphenyl aryl sulphonates.

No.	Aryl.	M.P./B.P.	%Yield.	Formula.	% Sulphur. Found.	Calc.
1.	4'-Fluorophenyl	85-86°	56.4	$C_{13}H_{11}O_3FS$	11.70	12.03
2.	2'-Methyl-5'-fluorophenyl	170-72°/30-35 mm	68.6	$C_{14}H_{13}O_3FS$	10.80	11.43
3.	4'-Fluoronaphthyl	59-60°	60.8	$C_{17}H_{13}O_3FS$	9.83	10.13

Hydroxydiaryl Sulphones.—A mixture of diaryl sulphonate (1 *M*) and anhydrous aluminium chloride (1.5*M*) was heated in an oil bath at 130-40° for 2 to 3 hours. The *o*-hydroxysulphones were isolated and purified in the usual manner. Analytical data, m.p., and yields of the compounds synthesised are recorded in Tables IV and V.

TABLE IV

2-Hydroxy-5-fluorophenylaryl sulphones.

No.	Aryl.	M.P.	%Yield.	Formula.	% Sulphur. Found.	Calc.
1.	4'-Methylphenyl	45°	39.5	$C_{13}H_{11}O_3FS$	11.63	12.03
2.	4'-Chlorophenyl	126-27°	44.4	$C_{12}H_8O_3ClFS$	10.85	11.17
3.	4'-Fluorophenyl	65-66°	43.0	$C_{12}H_8O_3F_2S$	11.08	11.85
4.	2',5'-Dichlorophenyl	84-85°	28.0	$C_{12}H_7O_3Cl_2FS$	10.02	9.97
5.	2',5'-Dibromophenyl	74-75°	16.2	$C_{12}H_7O_3Br_2FS$	7.31	7.80
6.	2'-Bromo-5'-fluorophenyl	103°	28.3	$C_{12}H_7O_3BrF_2S$	8.72	9.17
7.	2'-Methyl-5'-fluorophenyl	92-93°	49.0	$C_{13}H_{10}O_3F_2S$	10.63	11.27
8.	4'-Fluoronaphthyl	101-102°	10.5	$C_{16}H_{10}O_3F_2S$	9.40	10.00

TABLE V

2-Hydroxy-5-methylphenyl aryl sulphones.

No.	Aryl.	M.P.	%Yield.	Formula.	% Sulphur. Found.	Calc.
1.	4'-Fluorophenyl	72-73°	26.5	$C_{13}H_{11}O_3FS$	11.50	12.03
2.	2'-Methyl-5'-fluorophenyl	110°	27.6	$C_{14}H_{13}O_3FS$	10.86	11.43
3.	4'-Fluoro[illegible]yl	104-05°	13.5	$C_{17}H_{13}O_3FS$	9.54	10.13

The pe[illegible]ctivity of these compounds is under investigation and will be communicated in due course.

The authors express their grateful thanks to Dr. R. C. Mehrotra, Professor and Head of the Department of Chemistry, University of Gorakhpur, for providing necessary facilities.

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Received November 11, 1960

[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

Spectrophotometric Study of Chelate Formation by Interaction of Hexavalent Chromium and Alizarin Red S

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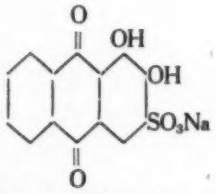
Formation of a pink-coloured complex by the interaction of Cr (VI) and sodium alizarin-3-sulphonate (Alizarin Red S) has been reported. The chelate has maximum absorption at 515 $m\mu$. The composition, as determined by the method of continued variation using spectrophotometric measurements, is indicated to be 1:1. The chelate is stable between pH 3.5 and 8.0. The stability has been determined by a method described by the authors and the values of $\log K$ and ΔF° work out respectively to be 4.72 ± 0.25 and -6.52 ± 0.35 kcal. at 25°.

Sodium alizarin-3-sulphonate, commonly known as Alizarin Red S (abbreviated as ARS), is a member of the anthraquinone series of dyes and yields coloured chelates with various metals (Dey and Mukherji, *Proc. Nat. Acad. Sci., India*, 1957, **26A,** 242; Dey and Banerji, Proc. Symp. Chemistry of Co-ordination Compounds, Agra, 1959). The presence of quinoid oxygen with hydroxyl groups in α and β positions is responsible for its chromophoric properties while the presence of a sulphonate group adds reactivity to the molecule. The structure of the compound is :



(Sodium alizarin-3-sulphonate)

Dey and co-workers studied the chromophoric properties of the reagent in detail and found it useful for the colorimetric determination of uranium (*Z. anal. Chem.*, 1958, **160,** 98) and of copper (*Bull. Chem. Soc., Japan*, 1958, **31,** 521). They also studied the characteristics of aqueous solutions of the reagent and found that the reagent behaved as a colloidal electrolyte (*Kolloid Z.*, 1958, **158,** 147). It was emphasised that for physico-chemical measurements, extremely dilute solutions should be employed so as to exhibit the characteristics of a true solution.

In further communications from these laboratories chelate formation of Alizarin Red S with lead (*Proc. Nat. Acad. Sci., India*, 1957, **26A,** 20), copper (this *Journal*, 1957, **34,** 461), thorium, and hafnium (unpublished) has been reported. Chelates involving the reagent have also been described by Raghava Rao *et al.* (*Anal. Chim. Acta*, 1955, **13,** 79, 142), Leibhafsky and Winslow (*J. Amer. Chem. Soc.*, 1938, **60,** 1776), Larsen and Hirozawa (*J. Inorg. Nucl. Chem.*, 1956, **3,** 198), and by others.

A spectrophotometric method for the determination of formation constants of coloured chelates has been described by Mukherji and Dey (*J. Inorg. Nucl. Chem.*, 1958, **6,** 314); the method has an advantage over that of Anderson *et al.* (*J. Amer. Chem. Soc.*, 1948, **70,** 1195; 1949 **71,** 909, 912) that it is applicable to systems where one of the interactants may be coloured. In the present communication, formation of the coloured chelates by the interaction of hexavent chromium and Alizarin Red S has been described.

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EXPERIMENTAL

An aqueous solution of B.D.H. Reagent grade Alizarin Red S was prepared without further purification. The solution was standardised by estimating the sulphur content. B.D.H. AnalaR potassium chromate was used and the concentration was checked by the iodometric method. Solutions were prepared in double distilled water and fresh solutions were used to avoid effects due to hydrolysis.

Spectrophotometric Measurements.—Spectrophotometric studies were done with a Unicam SP 500 spectrophotometer operated by a Dorans Mains unit working on 220v/50 cycles stabilised A.C. mains. Glass measuring cells of 10 mm thickness supplied with the instrument were used. The experiments were performed in an air-conditioned room maintaining $25° \pm 1°$. The solutions and the mixtures were kept in a Townson and Mercer thermostatic bath maintaining $25° \pm 0.01°$. The mixtures were kept for 30 minutes, before measurements, in the thermostat to attain equilibrium.

*p*H measurements were done with the help of L & N *p*H indicator, operated by 220v/50 cycles A.C. mains, with a glass electrode and a calomel reference electrode supplied by the same manufacturers. The meter was calibrated with a standard buffer and occasionally checked during measurements.

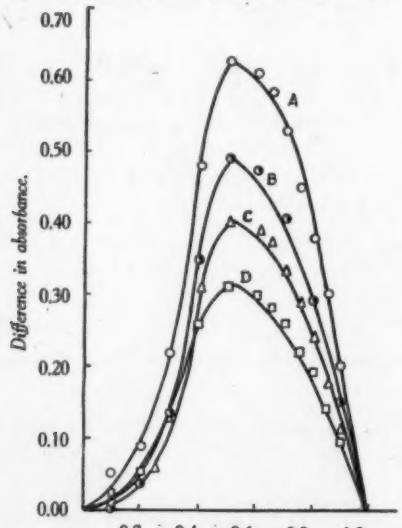
The maximum absorption of potassium chromate lies at 370 $m\mu$, that of alizarin red S at 420 $m\mu$ while a mixture of potassium chromate and the reagent has a maximum absorption at 515 $m\mu$. This shows the formation of a chelate between the interactants.

Stoichiometry of the Components

The composition was determined by Job's method of continued variation (*Compt. rend.*, 1925, **180**, 928). Measurements using both equimolecular and non-equimolecular solutions

FIG. 1

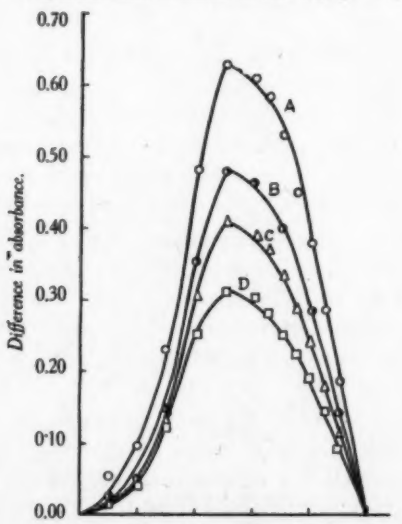
Equimolecular solutions at 515 $m\mu$ ($p = 1$).



Curve A: $c = 5.0 \times 10^{-4}M$. Curve B: $c = 4.0 \times 10^{-4}M$.
Curve C: $c = 3.33 \times 10^{-4}M$. Curve D: $c = 2.5 \times 10^{-4}M$.

FIG. 2

Equimolecular solutions at 525 $m\mu$ ($p = 1$)

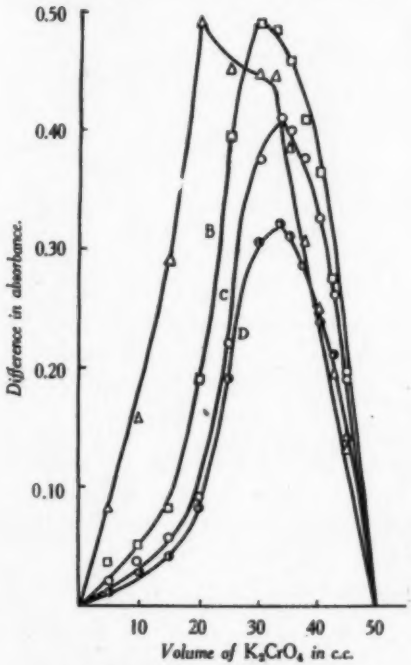


Concentrations the same as in Fig. 1.

in large number (total volume = 50c.c.) were done at two different wave lengths, viz., 515 and 525 mμ. This was necessary to ascertain definitely the composition of the complex (Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437). Some of the typical observations are plotted in Figs. 1-4. In the figures, the difference of absorbance of the mixture and that which would be shown by the chelating agent alone, in case of no reaction (chromate ions have no absorption at the wave lengths of measurement), is plotted against composition of the mixture.

FIG 3.

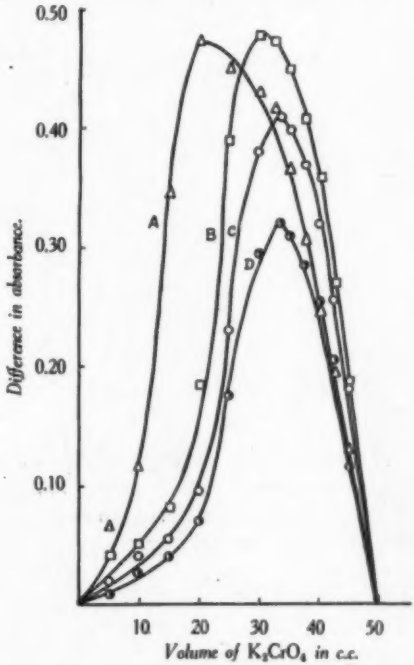
Non-equimolecular solutions at 515 mμ.



Curve A: $c = 5.0 \times 10^{-4}M$ ($\rho = 0.67$).
Curve B: $c = 3.33 \times 10^{-4}M$ ($\rho = 1.5$).
Curve C: $c = 2.5 \times 10^{-4}M$ ($\rho = 2.0$).
Curve D: $c = 2.0 \times 10^{-4}M$ ($\rho = 2.0$).

FIG. 4

Non-equimolecular solutions at 525 mμ.



Concentrations the same as in Fig. 3.

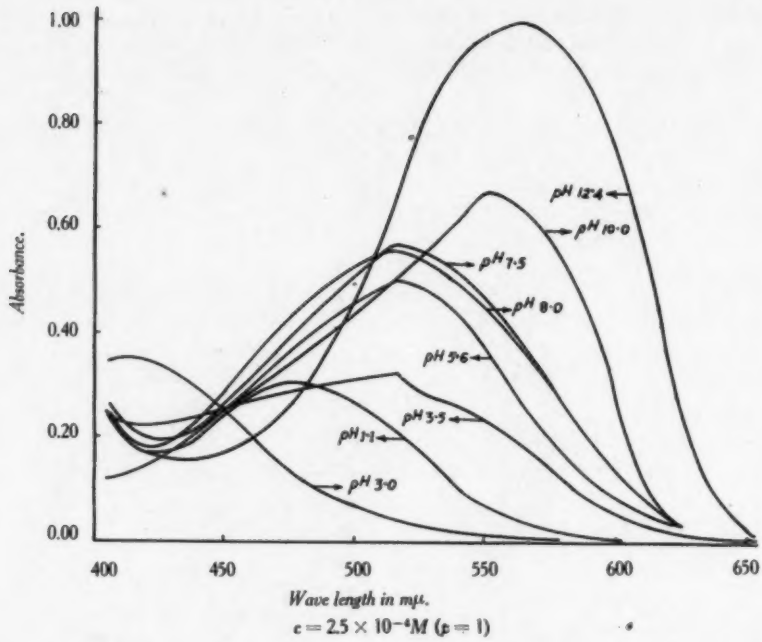
In the legends to the figures, the concentration of the chromate solution is represented by c, while c' is the concentration of Alizarin Red S; hence $\rho = c'/c$.

Influence of pH *on the Stability of the Chelate*

The absorbance of mixtures of 2.5×10^{-4} *M* potassium chromate and 2.5×10^{-4} Alizarin Red S at different *p*H was measured at different wave lengths. The results are represented in Fig. 5. It may be seen that the λ_{max} of the mixtures lie at 515 *m*μ between *p*H 3.5 and 8.0, showing that the chelate is stable in this range of *p*H.

FIG. 5

Influence of pH on absorbance.



$c = 2.5 \times 10^{-4} M$ ($p = 1$)

The following table records the results on the composition, arrived at from Figs. 1-4, indicating that the composition corresponds to 1 : 1. The table apparently reveals the composition in the case of non-equimolecular solutions also. Thus, it is not possible to calculate the stability from these curves by the method of continued variation.

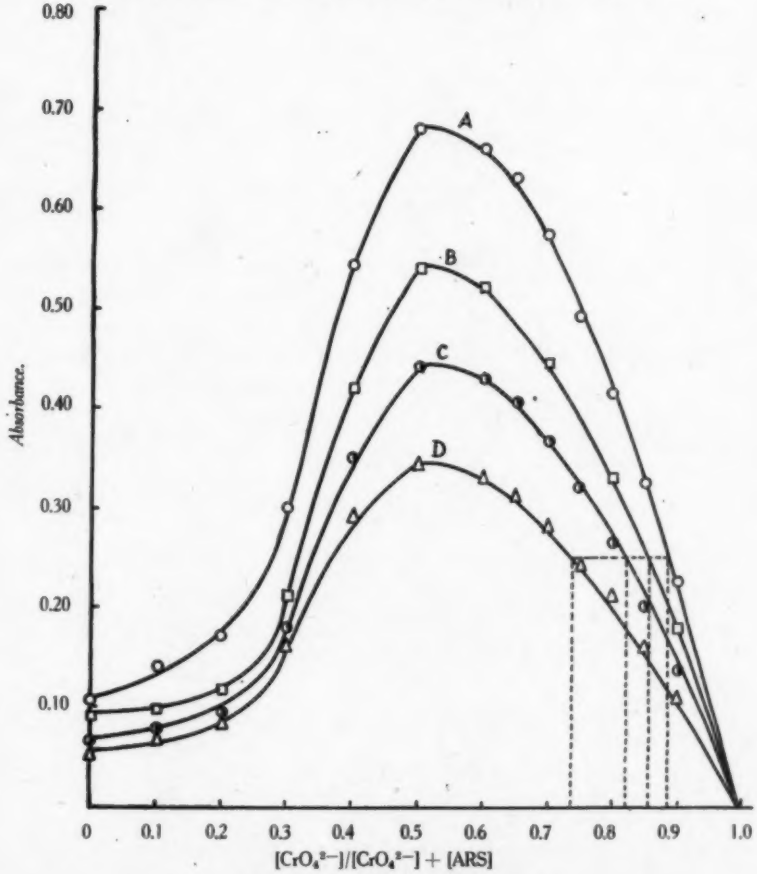
TABLE I

No. Fig.	Curve.	$c \times 10^4$.	p.	Wave length.	Peak occurring at volume of K_2CrO_4.	Composition of the chelate Cr(VI) : ARS.
1	A	5.00 *M*	1.0			
	B	4.00	1.0			
	C	3.33	1.0	515 mμ	25.0 c.c.	1:1
	D	2.50	1.0			
2	A	5.00	1.0			
	B	4.00	1.0			
	C	3.33	1.0	525	25.0	Do
	D	2.50	1.0			
3	A	5.00	0.67		20.0	
	B	3.33	1.50	515	30.0	Do
	C	2.50	2.00		33.3	
	D	2.00	2.00		33.3	
4	A	5.00	0.67		20.0	
	B	3.33	1.50	525	30.0	Do
	C	2.05	2.00		33.3	
	D	2.00	2.00		33.3	

The apparent formation constant of the chelate has been calculated from the observed absorbance-composition curves, as described earlier (this *Journal*, 1957, **34**, 461). In Fig. 6, in the descending portions of the curves A, B, C, and D, it may reasonably be assumed that the absorbance is due to the colour of the complex alone since chromate ions are colorless at the dilutions and at the wave length of measurement, and are in excess over the chelating agent, a majority of which therefore is bound up in the complex, which is fairly stable, and does not contribute substantially to the colour of the system. Thus, at concentrations of the reactants in curves A, B, C, and D, where the absorbance is the same (say 0.25), the amounts of the complex formed are identical.

FIG. 6

Formation constant from absorption spectra data at 515 mμ.



Concentrations the same as in Fig. 1

In an equilibrium of the type :

$$M + Ke \rightleftharpoons MKe$$

where M and Ke are the metal and the chelating agent respectively, x is the concentration of the chelate at equilibrium, and a and b are the initial concentrations of the metal ion and the chelating agent respectively, we have formation constant

$$K = \frac{x}{(a-x)(b-x)} \qquad \ldots \qquad (i)$$

Taking two concentrations having the same absorbance, *i.e.*, the same value of x, we have

$$K = \frac{x}{(a_2-x)(b_2-x)} = \frac{x}{(a_1-x)(b_1-x)} \qquad \ldots \qquad (ii)$$

or

$$x = \frac{a_1b_1 - a_2b_2}{(a_1+b_1)-(a_2+b_2)} \qquad \ldots \qquad (iii)$$

Hence from a knowledge of two initial concentrations, a_1, a_2 and b_1, b_2, we can calculate x from (*iii*). Knowing x, K can be evaluated from (*i*). The value of log K in this system works out to be 4.72 ± 0.25 at 25°.

The free energy of formation

$$\Delta F^\circ = -RT \ln K,$$

where the terms have their usual significance. In Cr(VI) — ARS system, ΔF° at 25° is found to be -6.53 ± 0.34 k cals.

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Received April 7, 1960.

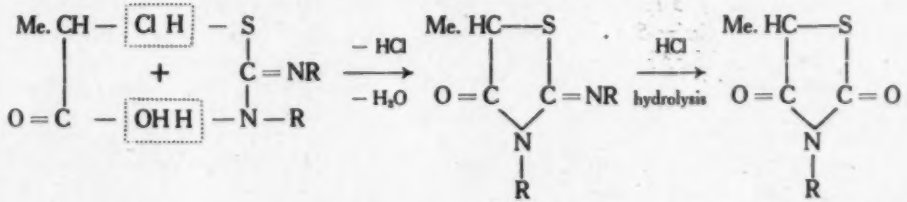
[Jour. Indian Chem. Soc., Vol. 38, No. 2, 1961]

Some New 2-Arylimino-3-aryl-5-methyl-4-thiazolidones and 3-Aryl-5-methyl-2,4-thiazolidiones

P. N. Bhargava and Phulgan Ram

Nine new 3-aryl-2-arylimino-5-methyl-4-thiazolidones have been prepared and twelve new 3-aryl-5-methyl-2,4-thiazolidiones have been synthesised. The products of their decomposition and hydrolysis have been identified.

In view of the significant biological properties of thiazolidones and thiazolidiones as inhibitors of electrically induced and metrazole induced convulsions, local anæsthetics, bactericides, and fungicides, preparations of some new 2-arylimino-3-aryl-5-methyl-4-thiazolidones (I) and 3-aryl-5-methyl-2,4-thiazolidiones (II) were taken up for biological studies (Bhargava *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 2353; this *Journal*, 1955, **32**, 49; 1956, **33**, 596; 1957, **34**, 475, 776). Thiazolidones have been obtained by the interaction of *sym.*-diaryl thioureas prepared from aniline, *o*-, *m*-, and *p*-toluidine, *m*-chloroaniline, *o*- and *p*-phenetidine, *o*-anisidine, and β-naphthylamine with α-chloropropionic acid in presence of anhydrous sodium acetate and absolute ethanol under conditions laid down by Bhargava *et al.* (*loc. cit.*) according to the reaction :



(I) (II)

The structure of the compound has been corroborated by its degradation products and characteristic derivatives obtained. 3-Phenyl-2-phenylimino-5-methyl-4-thiazolidone decomposes to *sym.*-diphenylurea and methylthioglycollic acid when refluxed with a strong solution of ethanolic KOH and to 3-phenyl-5-methyl-2, 4-thiazolidione when hydrolysed with HCl (conc.).

Similarly 3-aryl-5-methyl-2, 4-thiazolidiones have been obtained by the reaction of *sym.*-diaryl thiourea of aniline, *o*-, *m*-, and *p*-toluidine, *m*- and *p*-chloroaniline, *o*- and *p*-phenetidine, *o*- and *p*-anisidine, and α- and β-naphthylamines with α-chloropropionic acid in a mixture of glacial acetic acid and hydrochloric acid. 3-Phenyl-5-methyl-2, 4-thiazolidione on decomposition with KOH has yielded aniline.

EXPERIMENTAL

3-Phenyl-2-phenylimino-5-methyl-4-thiazolidone.—A mixture of diphenylthiourea (10 g.), α-chloropropionic acid (8 c.c.), fused sodium acetate (7 g.), and ethanol (50 c.c.) was refluxed on a water bath for 5 hours. After distilling ethanol, the substance was washed with water, when a gummy product was obtained. It solidified on keeping overnight in contact with water. It was crystallised from ethanol in a colorless form, m.p. 105°. (Found : S, 11.10. $C_{16}H_{14}ON_2S$ requires S, 11.34%).

Similarly other 3-aryl-2-arylimino-5-methyl-4-thiazolidones were prepared from different thioureas, as recorded in Table I.

TABLE I

3-Aryl-2-arylimino-5-methyl-4-thiazolidones.

Thioureas.	Reflux time.	Colour.	M.P.	Formula.	%Sulphur. Found.	Calc.
sym.-Diphenyl-	5 hrs.	Colorless	105°	$C_{16}H_{14}ON_2S$	11.10	11.34
sym.-Di-*o*-tolyl-	6	Do	110°	$C_{18}H_{18}ON_2S$	10.7	10.32
sym.-Di-*m*-tolyl-	6	Yellow	98°	$C_{18}H_{18}ON_2S$	10.78	10.32
sym.-Di-*p*-tolyl-	8	Colorless	160°	$C_{18}H_{18}ON_2S$	10.35	10.32
sym.-Di-*m*-chlorophenyl-	6	Do	122°	$C_{16}H_{12}ON_2Cl_2S$	9.5	9.11
sym.-Di-*o*-anisyl-	6	Do	150°	$C_{18}H_{18}O_3N_2S$	9.58	9.35
sym.-Di-*o*-phenetyl-	6	Do	130°	$C_{20}H_{22}O_3N_2S$	8.90	8.64
sym.-Di-*p*-phenetyl-	6	Brown	108°	$C_{20}H_{22}O_3N_2S$	8.24	8.64
sym.-Di-β-naphthyl-	18	Do	184°	$C_{24}H_{18}ON_2S$	8.41	8.37

Decomposition of 3-Phenyl-2-phenylimino-5-methyl-4-thiazolidone with KOH.—A mixture of 3-phenyl-2-phenylimino-5-methyl-4-thiazolidone (2 g.), *N*-ethanolic KOH (20 c.c.), and ethanol (15 c.c.) was refluxed for 3 hours ; the contents were poured into water and filtered. After washing free of alkali, the residue was crystallised from ethanol, m.p. 238-39°. The mixed m.p. with a pure specimen of *sym.*-diphenylurea remained undepressed.

The filtrate developed a greenish blue colour with sodium nitroprusside, which is characteristic of thioglycollic and alkylthioglycollic acids, thereby confirming the presence of α-methylthioglycollic acid.

Hydrolysis with Ethanolic HCl *to 3-Phenyl-5-methyl-2, 4-thiazolidione.*—3-Phenyl-2-phenyl-4-imino-5-methyl-4-thiazolidone (2 g.), ethanol (15 c.c.), and HCl (conc., 5 c.c.) were refluxed on a water bath for 6 hours. After distilling ethanol, the mixture was poured into water and filtered. The residue was washed with water, dried, and crystallised from ethanol, m.p. 80°. (Found : S, 15.55. $C_{10}H_9O_2NS$ requires S, 15.45%).

3-Phenyl-5-methyl-2, 4-thiazolidione.—A mixture of *sym.*-diphenylthiourea (12 g.), α-chloropropionic acid (12 c.c.), and glacial acetic acid (50 c.c.) was refluxed for 3 hours. The reaction mixture was poured into cold water and kept overnight. The solid obtained was washed with water and crystallised from ethanol, m.p. 80°. (Found : S, 15.17. $C_{10}H_9O_2NS$ requires S, 15.45%).

Similarly other 3-aryl-5-methyl-2, 4-thiazolidiones were prepared from different thioureas, as recorded in Table II.

TABLE II

3-Aryl-5-methyl-2,4-thiazolidiones.

Thioureas.	Reflux time.	Colour.	M.P.	Formula.	%Sulphur. Found.	Calc.
sym.-Diphenyl-	3	Yellow	80°	$C_{16}H_{13}O_2NS$	15.17	15.45
sym.-Di-*o*-tolyl-	3	Pink	105°	$C_{11}H_{11}O_2NS$	14.49	14.47
sym.-Di-*m*-tolyl-	3	Brown	120°	$C_{11}H_{11}O_2NS$	14.3	14.47
sym.-Di-*p*-tolyl-	5	Colorless	140°	$C_{11}H_{11}O_2NS$	14.47	14.47
sym.-Di-*m*-chlorophenyl-	3	Do	120°	$C_{16}H_9O_2NCIS$	13.61	13.25
sym.-Di-*p*-chlorophenyl-	5	Do	160°	$C_{16}H_9O_2NCIS$	12.99	13.25
sym.-Di-*o*-anisyl-	3	Brown	125°	$C_{11}H_{11}O_3NS$	13.96	13.50
sym.-Di-*p*-anisyl-	3	Do	180°	$C_{11}H_{11}O_3NS$	13.62	13.50
sym.-Di-*o*-phenetyl-	4	Colorless	130°	$C_{13}H_{13}O_3NS$	12.48	12.75
sym.-Di-*p*-phenetyl-	3	Do	70°	$C_{13}H_{13}O_3NS$	12.46	12.75
sym.-Di-α-naphthyl-	12	Brown	72°	$C_{14}H_{11}O_2NS$	12.51	12.46
sym.-Di-β-naphthyl-	12	Do	69°	$C_{14}H_{11}O_2NS$	12.76	12.46

Decomposition of 3-Phenyl-5-methyl-2, 4-thiazolidione.—The thiazolidione (1 g.) was boiled with 40% KOH (50 c.c.) on a water bath for 3 hours. The reaction mixture on distillation gave a liquid which was confirmed as aniline by preparation of its azo-β-naphthol derivative.

Thanks are due to Dr. G. B. Singh, Head of the Chemistry Department, and the authorities of the Banaras Hindu University for providing necessary facilities.

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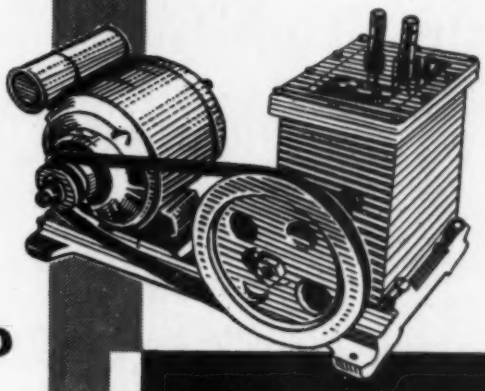

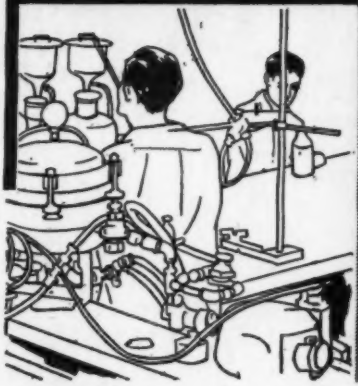

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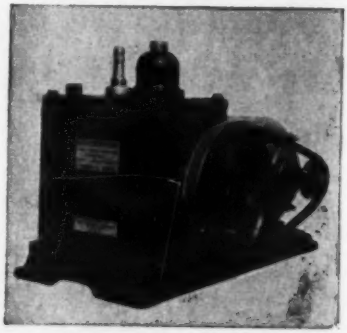

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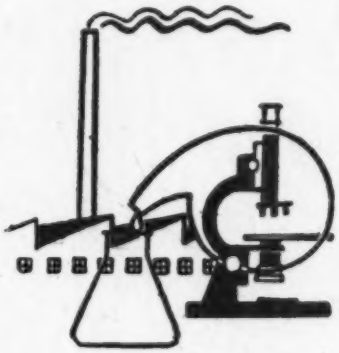

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